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pared with a standard instrument before use. Groschuff states (*Z. anorg. Chem.*, 1908, **58**, 108) that chromic anhydride supercools to the extent of 26°; our specimens, however, all solidified sharply within a degree or so of the m. p.

The viscosities of solutions of the anhydride were determined with an Ostwald viscometer as modified by Martin (*Bull. Soc. chim. Belg.*, 1925, **34**, 81). The instrument was standardised with conductivity water, and similar water, which had been stored in a Pyrex flask, was used for preparing the solutions. These were obtained by successive dilution. w is the weight of anhydride in 100 g. of water, η is the viscosity of the solution, and η_{H_2O} that of water (in dyne/cm.^{2}).

w.	η/η_{H_2O}.	η.	w.	η/η_{H_2O}.	η.
	Temp. 0°.			Temp. 25°.	
111·4	1·482	—	147·4	2·3360	0·02130
72·86	1·195	—	89·40	1·4880	0·01357
51·38	1·110	—	62·60	1·2480	0·01138
29·59	1·057	—	46·60	1·1600*	0·01058
			42·68	1·1360*	0·01036
	Temp. 18°.		31·67	1·0880	0·009923
98·98	1·5116	0·01616	24·36	1·0560	0·009631
71·01	1·2849	0·01373	12·05	1·024	0·009339
67·22	1·2674	0·01355			
49·59	1·1628	0·01243		Temp. 40°.	
35·92	1·1017	0·01178	111·4	1·328	0·008980
25·63	1·0581	0·01131	72·86	1·164	0·007871
16·71	1·0349	0·01106	51·38	1·1055	0·007475
			29·59	1·053	0·007120
			21·60	1·041	0·007039
			16·55	1·027	0·006945

The readings marked with asterisks appear to be 1—2% too high; they do not lie on the smooth curve passing through the other points. The figures for 40° are probably less trustworthy than those at the lower temperatures, as the thermostat was not automatically controlled at this temperature.

The absolute viscosities, η, were calculated with the aid of Leroux's values for the viscosity of water (*Ann. Physique*, 1925, **4**, 163). If these values are plotted on a very large scale, it is seen that Leroux's results for 2·5° (0·01648) and 7·5° (0·01419 dyne/cm.^{2}) are probably too high by about 0·00015 and 0·0002 dyne/cm.^{2}, respectively. The following equation, which is of the type proposed by Slotte (*Ann. Physik*, 1888, **34**, 28), represents the curve with fair accuracy between 10·9° and 30°:

$$\eta_{H_2O}\ (\text{dyne/cm.}^2) = \frac{0{\cdot}633161}{T - 241{\cdot}307} - 0{\cdot}00207155$$

where $T = t + 273$, t being in degrees Centigrade. The closeness of the observed and calculated values is of the order accepted by Thorpe and Rodger (*Phil. Trans.*, 1894, *A*, **185**, 397):

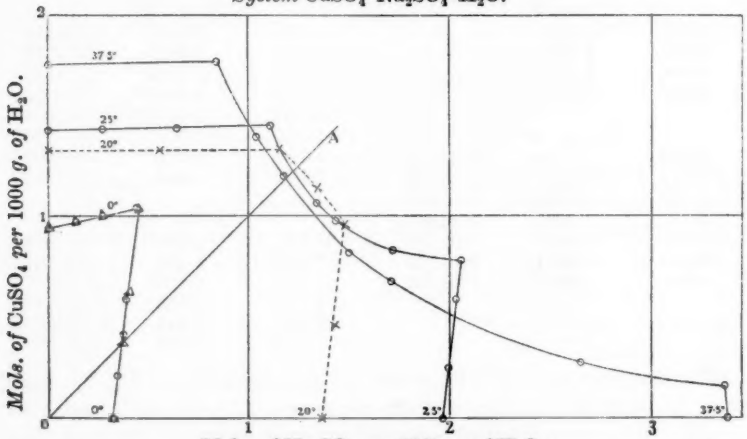
t.	η_{H_2O} (obs.).	(calc.).	t.	η_{H_2O} (obs.).	(calc.).
10·9°	0·01276	0·01279	20°	0·01018	0·010177
14	0·01175	0·01178	23·2	0·00949	0·00946
16	0·01121	0·01120	26·4	0·00883	0·008828
18	0·01069	0·01067	30	0·008198	0·008192

—East London College, London, E. 1. [*Received, October 6th*, 1927.]

Equilibrium in the System $CuSO_4$–Na_2SO_4–H_2O *at* 0°, 25°, *and* 37·5°. *A Correction.* By Robert Martin Caven and William Johnston.

An error appears in the figures relating to mols. of Na_2SO_4 per 1000 g. of H_2O (this vol., p. 2363), owing to the use of a wrong value for the

System $CuSO_4$–Na_2SO_4–H_2O.



Diacon's results at 0° *are indicated thus* △.
Massink's results at 20° *are indicated thus* ×, *and the isotherm by a broken line.*
0A *is the line of equimolecular proportions to show solubility of double salt.*

molecular weight of sodium sulphate. The correct figures are obtained by multiplying those given by the factor 0·838.

Fig. 4 on the same page needs a corresponding adjustment, and the correct figure is shown above.

The error now corrected does not invalidate the conclusions drawn in the paper.—Royal Technical College, Glasgow. [*Received, October 15th*, 1927.]

Change of Properties of Substances on Drying. By Herbert Brereton Baker.

My attention has been directed to a paper by D. Balarew (*J. pr. Chem.*, 1927, **116**, 57). The author sealed up various liquids in

U-tubes, a liquid in one limb and sublimed phosphorus pentoxide in the other, and kept them for 3½ years. He states that subsequent examination of all the liquids, which included hexane and benzene, showed the presence of phosphoric acid, and he suggests that the rise in boiling point which I have found may be due to the presence of this substance or its esters. Apart from the fact that the rise in boiling point which I mentioned (26° in the case of benzene, lately increased to 38°) could not be accounted for by the presence of such an impurity, it was distinctly stated in my paper (J., 1922, **121**, 572) that " In every case the liquid distilled from the dried apparatus was tested for the presence of phosphoric acid, and no trace could be detected." If Balarew's phosphorus pentoxide were not free from the volatile trioxide, his results could be understood.—IMPERIAL COLLEGE, LONDON, S.W. 7. [*Received, November 3rd*, 1927.]

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*The Dimorphism of 2-Chloroaceto-*p*-toluidide.* By MAURICE SCHOFIELD.

2-CHLORO-*p*-NITROTOLUENE (80 g.), m. p. 62·5°, obtained by chlorinating *p*-nitrotoluene (100 g.) at 57—59° in presence of anhydrous ferric chloride (4 g.) and in absence of sunlight and moisture, isolated by pouring the product into water, and crystallised from methylated spirit, was reduced at 60—70° with water (350 c.c.), iron powder (in slight excess; added during 2½ hours), and a little hydrochloric acid. The 2-chloro-*p*-toluidine thus obtained, b. p. 238—240°, m. p. 18°, was acetylated with acetic anhydride and acetic acid. The 2-chloroaceto-*p*-toluidide obtained (Found: C, 58·8; H, 5·5; N, 7·5. Calc. for $C_9H_{10}ONCl$: C, 58·8; H, 5·6; N, 7·6%) crystallised from benzene, alcohol, carbon disulphide, ether, and toluene in needles, m. p. 83°. This form, however, crystallised from light petroleum (b. p. 60—80°), in which it was sparingly soluble, in plates, m. p. 104°, and even when it was refluxed with a small quantity of this solvent a bulky, feathery mass, m. p. 104°, was obtained (Found: C, 58·7; H, 5·6; N, 7·7%). The reverse change was effected by crystallising the 104° form from benzene. After the molten 83° form had been kept at 120° for several minutes, solidification occurred at 93° after super-cooling to 89°. No crystallisation took place above 93° if the melt had been kept at 120° for longer periods. Freezing points up to 101° were given by a melt kept under similar conditions and seeded with the 104° form.

Kunckell and Lillig (*J. pr. Chem.*, 1912, **86**, 517) describe 2-chloroaceto-*p*-toluidide as crystallising from benzene in needles, m. p. 104°. —WOLVERHAMPTON AND STAFFORDSHIRE TECHNICAL COLLEGE, WOLVERHAMPTON. [*Received, October 8th*, 1927.]

CCCLXXXVII.—*The Complex Salts of Nickel with Various Aliphatic Diamines.*

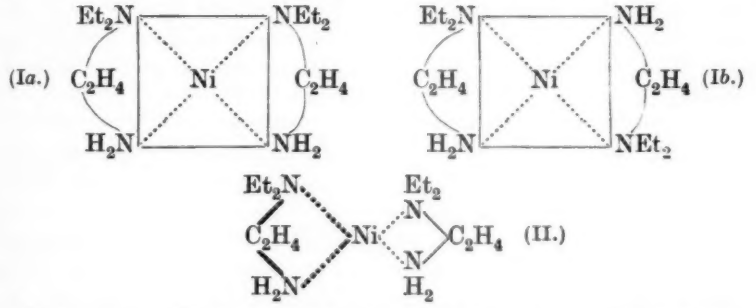
By Frederick George Mann.

Werner first suggested (*Z. anorg. Chem.*, 1893, **3**, 298) that when a metal shows a co-ordination number of 6, as in hexamminocobaltic chloride, $[Co(NH_3)_6]Cl_3$, the co-ordinated groups lie at the apices of a regular octahedron described around the metallic atom. The resolution into optically active forms of various complex salts of eight different metals (Co, Cr, Rh, Fe, Pt, Ir, Ru, and Al : also As), all having a co-ordination number of 6, leaves little doubt of the correctness of Werner's views.

Very great uncertainty still exists, however, with regard to the configuration of the complex salts of metals having a co-ordination number of 4, *e.g.*, tetramminonickelous chloride, $[Ni(NH_3)_4]Cl_2$. Biltz and Fetkenheuer (*Z. anorg. Chem.*, 1914, **89**, 121) claim to have prepared two distinct forms of the neutral non-ionic dichlorodiamminocobalt, $[Cl_2Co(NH_3)_2]$, and of the corresponding dibromo- and di-iodo-compounds, a result which would indicate that the four co-ordinated groups lie at the corners of a square with the metallic atom at the centre. This configuration would also explain the existence of two distinct forms of nickel iodate dihydrate, $[(H_2O)_2Ni(IO_3)_2]$ (Meusser, *Ber.*, 1901, **34**, 2438). Tschugaev (*Ber.*, 1906, **39**, 3192), however, failed to detect any similar *cis-trans*-isomerism in a series of salts such as bissuccinimidobismethylaminenickel, $[(C_4H_4O_2N)_2Ni(CH_3{\cdot}NH_2)_2]$. Moreover, the existence of the stable salts, $\beta\beta'\beta''$-triaminotriethylaminenickel thiocyanate, $[NiN(C_2H_4{\cdot}NH_2)_3](SCN)_2$, and $\gamma\gamma'\gamma''$-triaminotripropylaminenickel thiocyanate (Mann and Pope, J., 1926, 482, 489) is more easily explained by assuming that the four co-ordination valencies of the nickel atom are directed to the apices of a regular tetrahedron. Schlesinger (*Ber.*, 1925, **58**, 1877) found that copper, of co-ordination number 4, combines with certain bisimino-carboxylic acids to give compounds existing in two forms, and concludes that the copper complex has therefore the uniplanar configuration, a deduction opposed by Reihlen (*Z. anorg. Chem.*, 1926, **151**, 72), who considers the isomerism to be due to the presence of the two asymmetric nitrogen atoms in these compounds. Moreover, the recent resolution into optically active forms of 4-co-ordination derivatives of copper, zinc, and beryllium by Mills and Gotts (J., 1926, 3121) shows that such metallic complexes have the tetrahedral configuration, thus confirming the conclusions of Lowry and Burgess (J., 1924, **125**, 2081) with regard to the beryllium complex. On the other hand,

the existence of two forms of many derivatives of bivalent platinum and palladium, *e.g.*, dichlorodiamminoplatinum, $[Cl_2Pt(NH_3)_2]$, led Werner (*loc. cit.*, p. 310) to consider that here the complex was uniplanar and the two forms *cis-trans*-isomerides. Reihlen and Nestle (*Annalen*, 1926, **447**, 211) consider these compounds to be merely polymeric forms having the tetrahedral configuration,* a conclusion opposed on experimental grounds by Grunberg (*Z. anorg. Chem.*, 1926, **157**, 299) and Hantzsch (*Ber.*, 1926, **59**, 2761). Finally, the uniplanar configuration has been given to the dimethyltelluronium dihalides by Vernon (J., 1920, **117**, 90) to explain the existence of two isomeric forms.

Attempts were therefore made to obtain more decisive evidence with regard to the configuration of the 4-co-ordination nickel complex by preparing certain complex salts which, if possessing the uniplanar configuration, should show *cis-trans*-isomerism, and, if possessing the tetrahedral configuration, should be resolvable into optically active forms. Nickel was first combined with β-aminotriethylamine to give *bis-β-aminotriethylaminenickelous thiocyanate*, $[Ni\{(C_2H_5)_2N{\cdot}C_2H_4{\cdot}NH_2\}_2](SCN)_2$. This compound, if possessing the uniplanar configuration, should exist in the *cis* (I*a*)



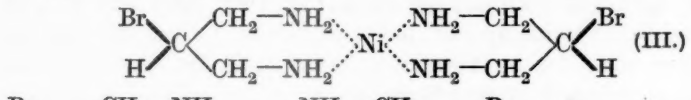
and the *trans* (I*b*) form, whilst if possessing the tetrahedral configuration (II),† it should be resolvable into optically active forms owing to its dissymmetric nature. No evidence of *cis-trans*-isomerism could be detected in this compound, whilst the presence of the tertiary nitrogen atoms rendered the complex so unstable that attempts at resolution could not be completed.

In order to avoid the presence of tertiary nitrogen atoms, a new type of complex salt was prepared by co-ordinating nickel with β-bromo-αγ-diaminopropane to give *bis-β-bromo-αγ-diaminopropane-*

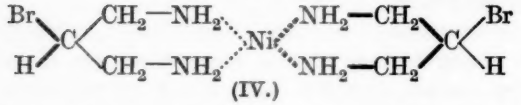
* Reihlen goes further and states (*Annalen*, 1926, **448**, 316) that all 4-co-ordination elements have the tetrahedral configuration.

† The thick bonds are in the plane of the paper, the thin ones at right angles to it.

nickelous thiocyanate, $[\{(NH_2\cdot CH_2)_2CHBr\}_2Ni](SCN)_2$. If this complex has the uniplanar configuration, the two co-ordinated ring systems lie in one plane, which is at right angles to that in which the terminal bromine and hydrogen atoms lie : the complex should therefore show *cis-trans*-isomerism according as the two bromine atoms are both on one side of the co-ordinated plane (III) or are on opposite sides, respectively. If, however, the complex has the



(III.)



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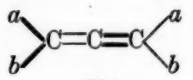


(V.)

tetrahedral configuration, the two ring systems are at right angles to each other (IV) : the complex thus possesses molecular dissymmetry, being structurally of the same type as the allene compounds (V), and should be resolvable into optically active forms. Here again, however, the highly crystalline dithiocyanate showed no signs of *cis-trans*-isomerism, whilst attempts at resolution failed because of the labile character of the bromine atoms; *e.g.*, the bis-β-bromo-αγ-diaminopropanenickelous thiocyanate in hot aqueous solution changed rapidly into the highly crystalline *bis-β-thiocyano-αγ-diaminopropanenickelous thiocyanate*,

$$[\{(NH_2\cdot CH_2)_2CH(SCN)\}_2Ni](SCN)_2.$$

Although this compound is of the required type for the purposes of this investigation, its low solubility in water made it unsuitable for use. Attempts were made to join a more stable group to the central carbon atom, and in particular to prepare αγ-diamino-*iso*propyl methyl ether, $(NH_2\cdot CH_2)_2CH\cdot O\cdot CH_3$. αγ-Dichlorohydrin reacts readily with potassium phthalimide to give αγ-diphthalimido-*iso*propyl alcohol, $(C_6H_4<^{CO}_{CO}>N\cdot CH_2)_2CH\cdot OH$: the hydroxyl group is, however, so well protected (probably sterically) that it is extremely inert and could not be methylated. Dichlorohydrin was itself methylated to give dichloro*iso*propyl methyl ether (Hess and Fink, *Ber.*, 1915, **48**, 2003), but the chlorine atoms were now extremely inert and would not react with potassium phthalimide even when heated in a sealed tube at 180° for 4 hours.

Nickel was next combined with the easily obtained αγ-diamino-*iso*propyl alcohol to give *bis-αγ-diamino-β-hydroxypropanenickelous thiocyanate*, $[\{(NH_2\cdot CH_2)_2CH\cdot OH\}_2Ni](SCN)_2$. Since, however, bivalent nickel may show a co-ordination number of 4 or of 6, it is difficult to decide whether in this compound the nickel has a

co-ordination number of 4 and is combined solely with the four amino-groups, or of 6 and is combined with the four amino-groups and with the two hydroxyl groups. It was found, however, that the diamine co-ordinates with cobalt to give *dihydroxybis-αγ-diamino-β-hydroxypropanecobaltic monochloride*,

$$[\{(NH_2\cdot CH_2)_2CH\cdot OH\}_2Co(OH)_2]Cl,$$

a compound in which the alcohol molecules must be co-ordinated by the amino-groups alone, and it was considered probable that the same held true of the above nickel compound, which should therefore be of the desired type. Again, however, no trace of *cis-trans*-isomerism was detected, and all attempts at resolution failed.

β-*Methyltrimethylenediamine* was now synthesised by converting β-methyltrimethylene dibromide into the corresponding *diphthalimido*-compound and hydrolysing it. The diamine was combined with nickel to give *bis-β-methyltrimethylenediaminenickelous thiocyanate*, $[\{CH_3\cdot CH(CH_2\cdot NH_2)_2\}_2Ni](SCN)_2$. This compound, although highly crystalline, showed no evidence of *cis-trans*-isomerism, and all attempts at resolution again failed.

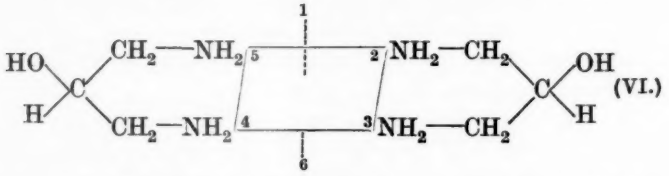
These repeated failures to resolve the nickel compounds may have been due either to the complex possessing the uniplanar configuration, or to the complex, if dissymmetric, undergoing such rapid racemisation that no evidence of resolution could be detected. The latter is presumably the reason for repeated failures in the past to resolve 6-co-ordination nickel derivatives, *e.g.*, trisethylenediaminenickel salts, and also tristriaminotriethylaminebisnickelous salts (Mann and Pope, *loc. cit.*, p. 486).

An interesting point arises here. It is well known that the complex compounds of nickel in which the metal has a co-ordination number of 4 are much more stable than those in which the co-ordination number is 6: yet nickel will combine with three molecules of the simplest aliphatic diamines, *e.g.*, ethylenediamine and propylenediamine, to give compounds such as trisethylenediaminenickel chloride, $[Ni\,en_3]Cl_2$, which are sufficiently stable to be isolated and sometimes even recrystallised, in spite of the fact that the metal here has a co-ordination number of 6. Yet in the present investigation it was found that even if a nickel salt (nickel chloride in aqueous solution: nickel succinimide in alcoholic solution) was treated with a very large excess of the various diamines employed, *viz.*, β-aminotriethylamine, αγ-diamino*iso*propyl alcohol, and β-methyltrimethylenediamine, only two molecules of the diamine co-ordinated with the metal and no trace of a compound in which the metal had a co-ordination number of 6 could be isolated. Similarly *roseo*cobaltic chloride on treatment with a large excess of diamino*iso*propyl alcohol gave always dihydroxybisdiaminohydroxy-

propanecobaltic monochloride, and again no compound in which three molecules of the diamine co-ordinated with the cobalt atom could be prepared. Many similar instances have previously been recorded. Thus nickel combines with only two molecules of dimethylglyoxime, to give $[Ni(ON{:}CMe{\cdot}CMe{:}N{\cdot}OH)_2]$, and never with three molecules, whilst cobalt will give diamminobisdimethylglyoximecobaltic monochloride, $[(ON{:}CMe{\cdot}CMe{:}N{\cdot}OH)_2Co(NH_3)_2]Cl$, but will not combine with three molecules of the dioxime. Dicyanodiamidine gives diaquobisdicyanodiamidinenickel,

$$[\{NH_2{\cdot}(NH{:})C{\cdot}N{\cdot}CO{\cdot}NH_2\}_2Ni(H_2O)_2],$$

but the two molecules of water cannot be replaced by a third molecule of the diamidine. This inability of nickel * to combine with more than two molecules of any but the simplest double-bridging groups cannot be ascribed to the general instability of 6-co-ordination nickel compounds, since tristriaminotriethylaminebisnickelous tetraiodide is a very stable compound, in spite of the presence of two weakly co-ordinating aliphatic tertiary nitrogen atoms : it is more probably due to the difficult access of the third molecule of the diamine. Thus if, when nickel is treated with an excess of, *e.g.*, diamino*iso*propyl alcohol, two molecules of the diamine co-ordinate first to give a 4-co-ordination complex having the uniplanar configuration (VI), co-ordination of a third molecule of the diamine



(VI.)

would involve bridging the potential 1 : 6-positions, which is structurally probably impossible. Similarly, with tervalent cobalt it is probable that the first two molecules of the diamine again occupy the 2 : 3- and 4 : 5-positions respectively; whence the distant 1- and 6-positions have to be occupied by simple unbridged groups as in dihydroxybisdiaminohydroxypropanecobaltic chloride and diamminobisdimethylglyoximecobaltic chloride.

Although the extreme difficulty of co-ordinating a third double-bridging group to the nickel atom can thus be explained on the assumption that the 4-co-ordination nickel complex has the uniplanar configuration, it is, on the other hand, significant that in the present investigation the five different complex salts showed no

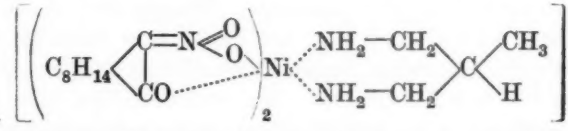
* Tervalent cobalt does not always share this inability : it will combine, *e.g.*, with 3 molecules of α-nitroso-β-naphthol (Morgan and Smith, J., 1921, **119**, 704).

evidence of *cis-trans*-isomerism, although all were highly crystalline compounds in which such isomerism should have been easily detected. The evidence for the configuration of the nickel complex thus remains conflicting.

A novel and apparently quite general reaction of 4-co-ordination nickel salts arose in the present investigation. Werner, in order to resolve certain complex salts of chromium (*Ber.*, 1912, **45**, 865), had recourse to crystallisation of the camphornitronates of the complex, prepared by simple double decomposition with the normal salts. Similar attempts were made with these nickel complex salts, since crystallisation of the camphorsulphonates had failed to effect resolution. When, however, bis-β-methyltrimethylenediaminenickelous nitrate is treated in cold aqueous solution with an excess of ammonium nitrocamphor, ammonia is at once liberated, the solution changes in colour from deep blue to green, and a rapid precipitation of the green, neutral, non-ionic *biscamphornitronate-β-methyltrimethylenediaminenickel* occurs, in accordance with the equation

$$[Ni\{CH_3{\cdot}CH(CH_2{\cdot}NH_2)_2\}_2](NO_3)_2 + 2C_{10}H_{14}O{\cdot}NO_2NH_4 = [(C_{10}H_{14}O{\cdot}NO_2)_2Ni\{CH_3{\cdot}CH(CH_2{\cdot}NH_2)_2\}] + CH_3{\cdot}CH(CH_2{\cdot}NH_2,HNO_3)_2 + 2NH_3.$$

A precisely similar reaction occurs with the corresponding compounds of β-aminotriethylamine and diamino*iso*propyl alcohol, thus providing further evidence that the latter diamine occupies only two co-ordination positions, *i.e.*, is co-ordinated by the amino-groups alone and not by the hydroxyl group. The three compounds so obtained are soluble in the usual organic liquids, but insoluble in water, a property common to many neutral, non-ionic co-ordination compounds. It is probable that in these compounds the ketonic group in the camphor molecule is also linked by a subsidiary valency to the nickel atom, which has therefore a co-ordination number of 6 (VII). In this case the complex as a whole becomes



(VII.)

dissymmetric (in addition to the dissymmetric character of the constituent camphor residues) and the recrystallised compounds in solution might be expected to show mutarotation owing to slow racemisation of the complex itself. No such mutarotation was shown in chloroform solution, however, by the three compounds of this type available.

It is obvious that the new diamine, β-methyltrimethylenediamine, should prove extremely useful in the solution of various problems connected with the stereochemistry of complex salts. Its use will unfortunately be limited, because the preparation of β-methyltrimethylene dibromide is extremely slow and tedious and the yield of the diphthalimido-compound is very small owing to side reactions. The diamine, however, co-ordinates with bivalent platinum to give *bis-β-methyltrimethylenediamineplatinous chloride*, $[Pt\{CH_3{\cdot}CH(CH_2{\cdot}NH_2)_2\}_2]Cl_2$. This compound is now being further investigated, since the occurrence of *cis-trans*-isomerism or of optical activity would solve the vexed question of the configuration of the complex platinous salts.

Experimental.

All rotations given in this paper have been measured at 15° in a 4-dcm. polarimeter tube.

The Complex Salts of β-Aminotriethylamine.

β-Aminotriethylamine, $N(C_2H_5)_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$.—In view of the low solubility of phthal-β-bromoethylimide in diethylamine, Ristenpart's preparation of this base can with advantage be modified as follows : Phthal-β-bromoethylimide (23 g.), diethylamine (18·3 c.c.), and anhydrous xylene (50 c.c.) were confined in a round-bottomed bottle and heated at 100° for 10 hours, diethylamine hydrobromide slowly crystallising from the clear solution. The cold mixture was acidified with hydrochloric acid (1 : 1 by vol.), the xylene removed by steam distillation, and the residue hydrolysed by boiling under reflux, with the addition of fresh acid, for 3 hours. The product was then made alkaline and steam-distilled. The mixture of bases which separated when the distillate was saturated with potassium hydroxide was dried over fresh potash and then fractionally distilled. β-Aminotriethylamine was obtained as a colourless liquid, b. p. 144—146°.

Bis-β-aminotriethylaminenickelous Thiocyanate.—β-Aminotriethylamine (15·8 c.c.; 3 mols.) was added to a solution of nickel succinimide (15·0 g.) in hot absolute alcohol (500 c.c.), and the whole boiled under reflux for 4 hours. The cooled filtrate from the concentrated solution, when treated with an equal volume of a saturated alcoholic solution (90%) of potassium thiocyanate, yielded almost immediately the above *thiocyanate*, which, after 3 hours, was washed with water, alcohol, and ether (yield 10·4 g., *i.e.*, 68% calculated on the nickel taken). The yield was considerably decreased if the alcohol used in the preparation was not absolute, or if the above large excess of the amine was not employed. In spite of this excess,

no compound in which the nickel had combined with more than two molecules of the amine could be isolated. The thiocyanate crystallised from absolute alcohol in lilac-blue needles, m. p. 213—214° (decomp.) after shrinking at 204° (Found: C, 41·5; H, 8·0; N, 20·7; Ni, 14·4. $C_{14}H_{32}N_6S_2Ni$ requires C, 41·3; H, 7·9; N, 20·65; Ni, 14·4%).

The *chloroplatinate*, $[\{N(C_2H_5)_2\cdot C_2H_4\cdot NH_2\}_2Ni]PtCl_6$, was precipitated on addition of a solution of the thiocyanate (0·5 g.) in acetone (35 c.c.) to a solution of sodium chloroplatinate (0·9 g.) in water (5 c.c.) and acetone (30 c.c.), and was obtained, after being washed with water, acetone and ether, as an apricot-coloured powder, insoluble in boiling water and alcohol. It darkens at 165—168° and shrinks to a plastic rod at 179—181° (Found: C, 20·4; H, 4·6. $C_{12}H_{32}N_4Cl_6NiPt$ requires C, 20·6; H, 4·6%).

Attempted Preparation of the d-*Camphor-β-sulphonate of the Complex.*—Hot solutions of bisaminotriethylaminenickelous thiocyanate (5 g.) in alcohol (300 c.c.) and of silver *d*-camphorsulphonate (8·3 g.) in alcohol (100 c.c.) were mixed, boiled for 5 minutes, and filtered. The fine, very pale blue, crystalline precipitate deposited on cooling was difficult to filter off and recrystallise. Eventually, 1 g. portions were dissolved in a little boiling absolute alcohol, and the solutions filtered quickly. The filtrates deposited very pale blue (almost white) crystals, m. p. 175—176°. This very pale blue colour is characteristic of many neutral non-ionic nickel complex salts, such as nickel succinimide, $[(H_2O)_2Ni(NC_4H_4O_2)_2]$: the camphorsulphonate, moreover, in alcoholic solution gave no precipitate with sodium chloroplatinate, although the chloroplatinate of the complex $[\{N(C_2H_5)_2\cdot C_2H_4\cdot NH_2\}_2Ni]''$ is insoluble in alcohol. It is probable, therefore, that the camphorsulphonate radicals had entered the complex, and the nickel had thus increased its co-ordination number to 6, giving the neutral non-ionic *bis*-d-*camphorsulphonatebisaminotriethylaminenickel*,

$$[(C_{10}H_{15}O\cdot SO_3)_2Ni\{N(C_2H_5)_2\cdot C_2H_4\cdot NH_2\}_2]$$

(Found: N, 7·4; S, 8·4; Ni, 7·45. $C_{32}H_{62}O_8N_4S_2Ni$ requires N, 7·4; S, 8·5; Ni, 7·8%).

The d-α-*bromocamphor-π-sulphonate* was obtained from the thiocyanate (5 g. in hot alcohol, 300 c.c.) and silver *d*-α-bromocamphor-π-sulphonate (10·7 g. in alcohol, 150 c.c.), the conditions and difficulties of the preparation being similar to those described above. Also, for reasons similar to those mentioned above, the very pale blue product, m. p. 165—168° (decomp.), probably has the constitution $[(C_{10}H_{14}BrO\cdot SO_3)_2Ni\{N(C_2H_5)_2\cdot C_2H_4\cdot NH_2\}_2]$ (Found: N, 5·9; Ni, 6·7, 6·65. $C_{32}H_{60}O_8N_4S_2Br_2Ni$ requires N, 6·15; Ni, 6·4%).

The alcoholic solution from which this compound originally separated was concentrated and cooled, and the precipitate of the nickel complex compound filtered off. The filtrate was evaporated to dryness, and the residue twice recrystallised from benzene, from which the d-α-*bromocamphorsulphonate* of β-*aminotriethylammonium hydroxide*, $(C_{10}H_{14}OBr{\cdot}SO_3H,NH_2{\cdot}C_2H_4){\cdot}NH(C_2H_5)_2{\cdot}OH$ separated in white crystals, m. p. 80—82° (Found: C, 43·5; H, 7·4; N, 6·5; Br, 17·9. $C_{16}H_{33}O_5N_2BrS$ requires C, 43·15; H, 7·5; N, 6·3; Br, 17·95%). The identity of this compound was confirmed by mixed melting-point determinations with the product obtained by treating bromocamphorsulphonic acid in alcoholic solution with an excess of the base, evaporating the solution to dryness, and recrystallising the residue from benzene. The presence of this compound in the original preparation shows that further decomposition of the complex occurs in hot alcoholic solution, the diamine being split off from the metal and becoming partially neutralised by the sulphonic acid.

Bis-d-*camphornitronateaminotriethylaminenickel*,

$$[(C_{10}H_{14}O{\cdot}NO_2)_2NiN(C_2H_5)_2{\cdot}C_2H_4{\cdot}NH_2].$$

—Finely-powdered silver *d*-camphornitronate (4·5 g.) was added to a solution of bis-β-aminotriethylaminenickelous thiocyanate (3·0 g.) in boiling alcohol (300 c.c.). After being boiled for 10 minutes and filtered, the deep olive-green solution was evaporated under reduced pressure to small bulk, again filtered, and then diluted with a little hot water. The precipitate was recrystallised from hot aqueous alcohol (95%), and the product thus obtained in deep olive-green crystals, m. p. 258—260° (decomp.) after softening at 248° (Found: C, 54·9; H, 7·6; N, 9·8. $C_{26}H_{44}O_6N_4Ni$ requires C, 55·0; H, 7·8; N, 9·9%). A 0·212% solution in chloroform had $\alpha_{5461} + 2{\cdot}33°$, whence $[\alpha]_{5461} + 275°$, and $[M]_{5461} + 1560°$: this rotation remained unchanged for 20 hours.

The Complex Salts of β-Bromo-αγ-diaminopropane.

β-*Bromo-αγ-diaminopropane*, $(NH_2{\cdot}CH_2)_2CHBr$.—Gabriel's preparation of the dihydrobromide of this base (*Ber.*, 1889, **22**, 225) was modified as follows: A mixture of diphthalimido*iso*propyl alcohol (7·0 g.) and a saturated solution of hydrogen bromide in acetic acid (23 c.c.) was heated in a sealed tube at 100° for 30 hours with occasional shaking. After cooling, the precipitate was filtered off, washed with alcohol, and recrystallised from acetic acid, from which *αγ-diphthalimidoisopropyl bromide* separated in colourless crystals, m. p. 196—198° (Found: N, 6·6; Br, 19·2. $C_{19}H_{13}O_4N_2Br$ requires N, 6·8; Br, 19·3%). This compound was boiled under reflux with hydrobromic acid of constant b. p., and the clear solution

was chilled, filtered from phthalic acid, and evaporated until, on cooling, the dihydrobromide of β-bromo-αγ-diaminopropane crystallised. The latter, when washed with alcohol and dried, was pure.

Bis-β-bromo-αγ-diaminopropanenickelous Thiocyanate.—A solution of β-bromo-αγ-diaminopropane dihydrobromide (13·0 g.) in 15% aqueous sodium hydroxide (19·0 c.c.) was added to one of nickel succinimide (6·0 g.) in boiling alcohol (240 c.c.), the green colour of the nickel solution changing at once to blue. The solution was boiled for 15 minutes, filtered, reduced to small bulk, and treated with a saturated solution of potassium thiocyanate in 95% alcohol. The precipitate was filtered off after 2 hours and washed with water, alcohol and ether. The *thiocyanate* was thus obtained as a fine pink powder, m. p. 200—203° (decomp.) after shrinking and darkening at 160°. It is insoluble in all the usual organic liquids, and is decomposed by hot water (Found: C, 20·0; H, 3·8; Br, 33·2; Ni, 12·2. $C_8H_{18}N_6Br_2S_2Ni$ requires C, 20·0; H, 3·8; Br, 33·25; Ni, 12·2%). If this compound is kept in contact with the original solution for more than 2 hours, it becomes contaminated with deep blue crystals of *bis-β-thiocyano-αγ-diaminopropanenickelous thiocyanate*. The latter compound was obtained pure by boiling bis-β-bromo-αγ-diaminopropanenickelous thiocyanate with water, a deep blue solution being obtained. The concentrated solution on quick cooling gave a fine blue, crystalline powder, whilst the dilute solution on slow cooling gave deep blue, heavy prisms; both deposits, after being washed with water, alcohol and ether, had m. p. 247—248° (decomp.) (Found: C, 27·5, 27·6; H, 4·4, 4·3; S, 29·4; Ni, 13·4. $C_{10}H_{18}N_8S_4Ni$ requires C, 27·5; H, 4·15; S, 29·3; Ni, 13·4%).

αγ-Dichloro*iso*propyl methyl ether, $(CH_2Cl)_2CH{\cdot}O{\cdot}CH_3$, was obtained as a colourless liquid, b. p. 66·5—67°/24 mm., having a characteristic peppermint-like odour (Found: C, 33·5; H, 5·7. Calc. for $C_4H_8OCl_2$: C, 33·6; H, 5·6%). When it was heated with an excess of potassium phthalimide in a sealed tube at 180° for 4 hours, much remained unchanged and no diphthalimido-derivative could be isolated.

*The Complex Salts of αγ-Diamino*isopropyl *Alcohol.*

*αγ-Diamino*isopropyl *Alcohol Dihydrochloride,* $(CH_2{\cdot}NH_2,HCl)_2CH{\cdot}OH$.—Diphthalimido*iso*propyl alcohol, prepared by Gabriel's method (*Ber.*, 1889, **22**, 224), was boiled under reflux with concentrated hydrochloric acid; the clear solution obtained, when chilled, filtered, and evaporated, gave the pure crystalline dihydrochloride.

Dihydroxybis-αγ-diamino-β-hydroxypropanecobaltic Monochloride.—A solution of diamino*iso*propyl alcohol dihydrochloride (12·2 g.; 2 mols.) in 10% aqueous sodium hydroxide (59 c.c.) was added to a mixture of *roseo*-cobaltic chloride (10 g.) and water (150 c.c.), and the whole heated under reflux on a water-bath for 3 hours, ammonia being freely evolved. The solution was then boiled for 30 minutes, filtered, and evaporated until crystals appeared. After cooling, the latter were collected and recrystallised from hot water, the *cobaltic monochloride* separating in dark red needles (Found: C, 23·6; H, 7·2; N, 17·9; Cl, 11·6. $C_6H_{22}O_4N_4ClCo$ requires C, 23·3; H, 7·2; N, 18·1; Cl, 11·5%). If the original solution was treated with potassium thiocyanate before the chloride started to crystallise, the corresponding *monothiocyanate* separated; after recrystallisation from water, it was obtained in fine, dark red crystals, decomp. 240—250° after shrinking at about 230° (Found: C, 25·2; H, 6·7; N, 21·0. $C_7H_{22}O_4N_5SCo$ requires C, 25·3; H, 6·7; N, 21·1%). A solution of the pure chloride, when treated with potassium iodide, gave the *monoiodide*, which also recrystallised from water in deep red leaflets (Found: C, 18·1; H, 5·5; I, 31·5. $C_6H_{22}O_4N_4ICo$ requires C, 18·0; H, 5·5; I, 31·7%).

Bis-αγ-diamino-β-hydroxypropanenickelous Thiocyanate.—A solution of diamino*iso*propyl alcohol dihydrochloride (17 g.) in water (50 c.c.) was treated with 10% aqueous sodium hydroxide (80·5 c.c.), and the whole added to a solution of hydrated nickel chloride (12 g.) in water (100 c.c.). The solution so obtained was heated under reflux on a water-bath for 4 hours, filtered, and concentrated. The addition of potassium thiocyanate solution gave the *thiocyanate* as a violet precipitate, which separated from hot water as a pale violet, crystalline powder, m. p. (to a clear blue liquid) 161—163° after shrinking at 105° (Found: C, 27·2; H, 5·6; N, 23·4; Ni, 16·7. $C_8H_{20}O_2N_6S_2Ni$ requires C, 27·1; H, 5·7; N, 23·7; Ni, 16·5%).

The original solution, when diluted with potassium iodide solution, slowly deposited the corresponding *di-iodide*, which separated from water, in which it was very soluble, in deep bluish-violet crystals, m. p. 239—242° (decomp.) (Found: C, 14·7; H, 4·1; I, 51·4. $C_6H_{20}O_2N_4I_2Ni$ requires C, 14·6; H, 4·1; I, 51·5%).

Bis-αγ-diamino-β-hydroxypropanenickelous d-*Camphor-β-sulphonate*, $[\{(CH_2{\cdot}NH_2)_2CH{\cdot}OH\}_2Ni](C_{10}H_{15}O{\cdot}SO_3)_2$.—Hot aqueous solutions of the thiocyanate (10 g.) and of silver *d*-camphorsulphonate (19·2 g.) were mixed, boiled for 5 minutes, filtered, and evaporated to dryness. The powdered residue was recrystallised from alcohol (charcoal), and the d-*camphor-β-sulphonate* obtained in pale lilac-blue crystals (Found: N, 8·2, 8·1; Ni, 8·6. $C_{26}H_{50}O_{10}N_4S_2Ni$ requires N, 8·0; Ni, 8·4%).

This camphorsulphonate was recrystallised seven times from alcohol, and its rotation for the mercury violet line (the only light which would penetrate the deep violet solutions) was then compared with those of the actual specimens of highly purified zinc and magnesium dicamphorsulphonates which Graham (J., 1912, **101**, 746) had prepared for rotatory determinations. The following readings were all made at 15° in a 4-dcm. tube. $\lambda = 4062$; c = concentration of the solution in g./100 c.c.; A denotes $C_{10}H_{15}O{\cdot}SO_3$.

Substance.	c.	α.	$[\alpha]$.	$[M]$.
$[\{(CH_2{\cdot}NH_2)_2CH{\cdot}OH\}_2Ni]A_2$ ...	1·7466	+3·60°	+51·5°	+361°
$MgA_2,6H_2O$	1·8824	+4·60	+61·1	+363
$ZnA_2,6H_2O$	1·8699	+4·25	+56·8	+361

These results show that the activity of the complex nickel salt is due solely to the camphorsulphonate radicals, and not to the complex itself. This was confirmed by reconverting the camphorsulphonate into the thiocyanate: the latter was inactive.

Bis - d - *camphornitronate* - $\alpha\gamma$ - *diamino* - β - *hydroxypropanenickel*, $[(C_{10}H_{14}O{\cdot}NO_2)_2Ni\{(CH_2{\cdot}NH_2)_2CH{\cdot}OH\}]$.—Hot aqueous solutions of the above thiocyanate and of silver nitrate (2 mols.) were mixed, boiled for 5 minutes, filtered, concentrated and chilled, a solution of the very soluble bis-$\alpha\gamma$-diamino-β-hydroxypropanenickelous nitrate being thus obtained. The addition of a concentrated cold aqueous solution of ammonium nitrocamphor (2·5 mols.) caused the violet colour to change immediately to green, and the solution, after 12 hours, deposited a fine, green precipitate. This, when dry, was soluble in nearly all the usual organic solvents: it was finally recrystallised from anhydrous benzene, from which *bis*-d-*camphornitronate*-$\alpha\gamma$-*diamino*-β-*hydroxypropanenickel* separated as a fine, olive-green powder with a molecule of benzene of crystallisation (Found: C, 56·5; H, 7·2; Ni, 9·3; C_6H_6, 12·3. $C_{29}H_{44}O_7N_4Ni$ requires C, 56·25; H, 7·2; Ni, 9·5; C_6H_6, 12·6%), which was lost in a vacuum at 80°, leaving the pure product as an olive-green powder; this shrank and blackened up to 210° (Found: C, 51·2; H, 7·0; Ni, 10·8. $C_{23}H_{38}O_7N_4Ni$ requires C, 51·0; H, 7·05; Ni, 10·85%). A 0·272% solution of the benzene-free material in chloroform had $\alpha_{5461} + 2{\cdot}89°$, whence $[\alpha]_{5461} + 266°$ and $[M]_{5461} + 1440°$. No change in rotation occurred during 20 hours.

The Complex Salts of β-*Methyltrimethylenediamine.*

$\alpha\gamma$-*Diphthalimido*-β-*methylpropane*, $CH_3{\cdot}CH(CH_2{\cdot}N{:}C_2O_2{:}C_6H_4)_2$.—A uniform mixture of potassium phthalimide (32 g.) and β-methyltrimethylene dibromide (Faworski, *Annalen*, 1907, **354**, 384) (10 c.c.) was heated at 175—180° for 6 hours. The cold product was pulverised and extracted twice with boiling carbon tetrachloride

(200 + 80 c.c.), giving 16 + 1·5 g. of the crude diphthalimido-compound and leaving a residue of potassium bromide and a small quantity of phthalimide. The phthalimido-compound was twice crystallised from boiling alcohol (400 c.c. each time), and *αγ-diphthalimido-β-methylpropane* obtained in fine, white, crystalline scales, m. p. 169—171° (Found: C, 68·8; H, 4·8; N, 8·1. $C_{20}H_{16}O_4N_2$ requires C, 68·9; H, 4·6; N, 8·05%).

β-Methyltrimethylenediamine Dihydrochloride, $CH_3{\cdot}CH(CH_2{\cdot}NH_2,HCl)_2$.—αγ-Diphthalimido-β-methylpropane (12 g.) and concentrated hydrochloric acid (50 c.c.), heated in a sealed tube at 160° for 18 hours, the tube being inverted from time to time to mix the contents, gave a clear pale brown solution; this, when cold, was filtered from phthalic acid and concentrated. The *dihydrochloride* was now obtained in three successive crops by (*a*) crystallisation from the concentrated aqueous solution, (*b*) diluting the filtrate from the first crop with alcohol, and (*c*) further dilution with ether [Found: (*a*) Cl, 43·9, (*b*) C, 29·8; H, 8·7; Cl, 44·0, (*c*) Cl, 43·9. $C_4H_{14}N_2Cl_2$ requires C, 29·8; H, 8·8; Cl, 44·0%]. It separated in deliquescent, fine, white crystals, m. p. 195—197°, very soluble in water, but insoluble in alcohol and ether.

The *dihydrobromide* was similarly obtained by means of concentrated hydrobromic acid, and separated, when the final concentrated solution was diluted with alcohol, in colourless needles, m. p. 227—229° (decomp.) (Found: Br, 64·0. $C_4H_{14}N_2Br_2$ requires Br, 64·0%).

The *dibenzoyl* derivative, $CH_3{\cdot}CH(CH_2{\cdot}NHBz)_2$, prepared in the usual way, after crystallising twice from benzene and once from acetone, was obtained in fine, white crystals, which melted with effervescence at 92—93°, rapidly resolidified, and remelted at 136—138° (Found: C, 73·2; H, 6·85. $C_{18}H_{20}O_2N_2$ requires C, 73·0; H, 6·8%).

Bis-β-methyltrimethylenediaminenickelous Thiocyanate.—A mixture of a solution of β-methyltrimethylenediamine dihydrochloride (9·0 g.; 2·2 mols.) in 10% aqueous sodium hydroxide (20 c.c.) with a solution of nickel succinimide (10 g.) in boiling alcohol (300 c.c.) rapidly became blue. It was boiled under reflux for 1 hour, filtered from a small quantity of an apple-green precipitate, and concentrated. The cold solution, on treatment with a concentrated aqueous solution of potassium thiocyanate, rapidly gave a bluish-red precipitate of the thiocyanate of the nickel complex. The latter can be recrystallised quickly from hot water, but prolonged boiling causes the precipitation of a green sludge. After two recrystallisations, the *thiocyanate* was obtained in deep blue needles,

m. p. 226—228° (decomp.) (Found: C, 33·9; H, 6·9; N, 24·0. $C_{10}H_{24}N_6S_2Ni$ requires C, 34·2; H, 6·9; N, 23·9%).

Bis-β-*methyltrimethylenediaminenickelous* d-*Camphor*-β-*sulphonate*, $[Ni\{CH_3{\cdot}CH(CH_2{\cdot}NH_2)_2\}_2](C_{10}H_{15}O{\cdot}SO_3)_2$.—Solutions of the above thiocyanate (6 g.) in hot water (120 c.c.) and of silver *d*-camphorsulphonate (11·8 g.) in water (100 c.c.) were slowly mixed and then boiled for 5 minutes. Filtration gave a clear blue solution which, when concentrated and chilled, furnished the d-*camphorsulphonate* in fine, lilac-blue scales. These were recrystallised twice from alcohol, and then had m. p. 287—288° (decomp.) (Found: C, 48·5; H, 7·7; N, 8·05; Ni, 8·4. $C_{28}H_{54}O_8N_4S_2Ni$ requires C, 48·2; H, 7·8; N, 8·0; Ni, 8·4%). This material was recrystallised seven times from alcohol, and so obtained as pale blue, minute crystals (Found: C, 48·3; H, 7·7%): a 1·098% aqueous solution had $\alpha_{4062} + 2{\cdot}11°$, whence $[\alpha]_{4062} + 48{\cdot}0°$ and $[M]_{4062} + 335°$. This sulphonate was reconverted in cold aqueous solution into the thiocyanate, which was inactive. A further preparation of the camphorsulphonate was recrystallised six times from water, and so obtained as the *monohydrate* (Found: C, 46·8; H, 8·2.

$$C_{28}H_{54}O_8N_4S_2Ni,H_2O$$

requires C, 47·0; H, 7·9%): this, in 1·059% aqueous solution, had $\alpha_{4062} + 2{\cdot}17°$, whence $[\alpha]_{4062} + 51{\cdot}2°$ and $[M]_{4062} + 366°$, but once again furnished an inactive thiocyanate.

Bis-d-*camphornitronate*-β-*methyltrimethylenediaminenickel*, $[(C_{10}H_{14}O{\cdot}NO_2)_2Ni\{CH_3{\cdot}CH(CH_2{\cdot}NH_2)_2\}]$.—A solution of the *d*-camphorsulphonate (5 g.) in water (50 c.c.) was treated with an excess of ammonium nitrocamphor (3·5 g.), also dissolved in water (25 c.c.). A green precipitate rapidly appeared, and the solution smelt strongly of ammonia. The precipitate was washed with water and recrystallised from alcohol, from which the *nitronate* separated in fine, olive-green crystals, m. p. 293—295° (decomp.) (Found: C, 53·4; H, 7·4; Ni, 10·8. $C_{24}H_{40}O_6N_4Ni$ requires C, 53·4; H, 7·5; Ni, 10·9%). A 0·273% solution in chloroform had $\alpha_{5461} + 3{\cdot}52°$, whence $[\alpha]_{5461} + 322°$ and $[M]_{5461} + 1736°$: the activity remained unchanged for 24 hours. This compound is only slightly soluble in water, but is soluble in nearly all the usual organic solvents.

The Complex Salts of β-*Methyltrimethylenediamine with Bivalent Platinum*.—A solution of ammonium chloroplatinite (4 g.) in water (20 c.c.) was added to one of methyltrimethylenediamine dihydrochloride (5·4 g.; 3 mols.) in 10% aqueous sodium hydroxide (12·8 c.c.). A pale yellow precipitate slowly separated, and after 2 hours the mixture was heated under reflux on a water-bath for a further 8 hours, and then chilled. The precipitate was filtered off and recrystallised from hot water, from which *dichloro*-β-*methyltri*-

methylenediamineplatinum, $[Cl_2Pt\{CH_3\cdot CH(CH_2\cdot NH_2)_2\}]$, separated in very pale yellow crystals, m. p. 273—276° (decomp.) (Found: C, 13·5; H, 3·45; Pt, 55·0. $C_4H_{12}N_2Cl_2Pt$ requires C, 13·5; H, 3·4; Pt, 55·1%). The original filtrate was now evaporated to about half its original volume, and on quick cooling, *bis*-β-*methyltrimethylenediamineplatinous chloride*, $[Pt\{CH_3\cdot CH(CH_2\cdot NH_2)_2\}_2]Cl_2$, separated as a fine, white, crystalline powder, m. p. 266—267° (decomp.) after darkening at about 240° (Found: C, 21·4; H, 5·45; Pt, 44·2. $C_8H_{24}N_4Cl_2Pt$ requires C, 21·7; H, 5·5; Pt, 44·1%). The filtrate, on standing several days, deposited a mixture of colourless crystals of sodium chloride and very pale yellow crystals of the platinous dichloride compound. The latter could be very easily separated by hand, and no indication of *cis-trans*-isomeric forms could be detected.

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CCCLXXXVIII.—*The Nature of the Alternating Effect in Carbon Chains. Part XXII. An Attempt further to define the Probable Mechanism of Orientation in Aromatic Substitution.*

By CHRISTOPHER KELK INGOLD and FLORENCE RUTH SHAW.

RECENT studies of reactivity transmission have led to the recognition in aromatic substitutions of orienting effects originating in the following combinations of inductively propagated electronic strain (I,⟶) and tautomeric or electromeric transformations (T,↷)* (for summary see *Ann. Reports*, 1926, p. 129):

Type				
Symbol	(1) $+I$	(2) $-I$	(3) $-I+T$	(4) $+I+T$
Examples	Toluene.	Phenylammonium ions. Phenylsulphones.	Halogenobenzenes. Phenylthionium ions.	Phenoxide ion.

On the other hand, previous results provide little positive information with regard to the paths whereby the effects thus arising traverse the nucleus. It is possible that the inductive and the

* For reasons given elsewhere, the possible combinations represented by $+I-T$ and $-I-T$ will not here be separately discussed, and it is also unnecessary for our present purpose to consider superimposed polar orientation through space.

tautomeric disturbances travel by different routes and influence the reactivity in the various positions of the nucleus in different relative degrees. The one clearly established circumstance is that both types of disturbance affect primarily the ortho- and para-positions.

The paucity of information on this subject is partly due to the fact that a knowledge of the proportions in which isomerides are formed in substitutions furnishes only one of the two kinds of data which are necessary for an analysis of the influence of orienting groups on the reactivity in each nuclear position. The other, consisting of the relative velocities of the total substitutions ($o + m + p$) of different substances, is, in general, not available. In this paper, a preliminary analysis of certain cases is attempted with the aid of new experimental data.

Before proceeding to details, it is desirable to define the terms employed. By the phrase "the reactivity in a given nuclear position" is meant the velocity, relative to some standard, of the substitution which occurs in that position under the conditions of the comparison. The effect of an orienting group on the reactivity of each nuclear position may therefore be defined as the number of molecules substituted during a small element of time at the given nuclear carbon atom, divided by the number which would have been substituted during the same element of time at the same carbon atom had the orienting group been absent. This ratio may be termed the "coefficient of activation" (F) for the orienting group and the nuclear position considered.

The results recorded below refer to nitration. It is, of course, certain that the relative reactivities of different nuclear carbon atoms will be found to vary with the nature of the substitution studied (*e.g.*, nitration and mercuration). Nevertheless there are good grounds for the belief that the broad, qualitative conclusions (which alone it is desired to indicate in this preliminary communication) will be found to apply, without serious alteration, to the behaviour of the nucleus in a large class of substitution reactions.

Case 1. *Type* + I. *Example: Toluene.*—Toluene is nitrated to the extent of approximately 59% in its ortho-positions, 4% in its meta-positions, and 37% in its para-position. The disparity between the *op*-substitution on the one hand and *m*-substitution on the other is universally regarded as indicating the *op*-orienting tendency of the methyl group; but it may have arisen in various ways. For instance, the orienting group may have caused an increase in *op*-reactivity accompanied by a decrease of *m*-reactivity (alternation, in fact); or it may have given rise to an increase of

op-reactivity, and left the *m*-position unaffected; or it may have produced a large increase in *op*-reactivity and a smaller increase in *m*-reactivity; and there are other possibilities. Actually each of the three alternatives mentioned has been assumed or implied in one or other of the theories of aromatic substitution which have been under discussion in recent years.

It is known from Wibaut's experiments (*Rec. trav. chim.*, 1915, **34**, 241) that toluene nitrates much more rapidly than benzene; but this does not decide the question at issue. Our study of the relative velocities of nitration of benzene and toluene has led to the conclusion that whilst the reactivity of each ortho- or para-carbon atom in toluene is increased roughly 30-fold, that of each meta-carbon atom is increased 2-fold by the directive action of the methyl group.

Benzene and toluene, both in excess, were nitrated together in a homogeneous solution; the reaction was allowed to proceed to completion and the product analysed. This method has an advantage over the alternative of carrying out parallel nitrations with benzene and toluene separately, inasmuch as uncertainties arising from imperfect, and consequently unequal, temperature control are avoided. The molecular ratio, R, in which the hydrocarbons are nitrated is not the ratio of the velocities, *ceteris paribus*, of the respective total substitutions, but may be used to determine it as follows.

It is assumed that the reactions are carried out in unit volume which does not change appreciably during the process. If x_0, y_0, and z_0 are the initial amounts of benzene, toluene, and nitric acid, respectively, and x and y are the quantities of benzene and toluene remaining after a time t, then at any moment

$$-dx/dt = k_x x\{x + y - (x_0 + y_0) + z_0\}$$

and

$$-dy/dt = k_y y\{x + y - (x_0 + y_0) + z_0\}.$$

These equations assume that the reactions are bimolecular and irreversible. This has been shown to be the case for the nitration of a considerable number of substances, including benzene, nitrobenzene, chlorobenzene, *op*-dinitrotoluene, and the three nitrobenzoic acids (Holleman and de Bruyn, *Rec. trav. chim.*, 1900, **19**, 79, 188, 364; 1901, **20**, 206, 352; Martinsen, *Z. physikal. Chem.*, 1905, **50**, 385; 1907, **59**, 605; Wibaut, *loc. cit.*). Phenol, however, is an exception, which is not surprising (Martinsen, *loc. cit.*; Klemenc, *Monatsh.*, 1914, **35**, 85; Arnall, J., 1923, **123**, 3111).

The above equations on simultaneous integration give

$$k_y/k_x = (\log y_\infty - \log y_0)/(\log x_\infty - \log x_0)$$

where x_∞ and y_∞ are the ultimate values of x and y, respectively. The two equations necessary to evaluate x_∞ and y_∞ are

$$x_\infty + y_\infty = x_0 + y_0 - z_0$$

and

$$R = (y_0 - y_\infty)/(x_0 - x_\infty),$$

and the final expression for the ratio of the velocities of the total substitutions is

$$\frac{k_y}{k_x} = \log\left\{1 - \frac{z_0}{y_0}\left(\frac{R}{1+R}\right)\right\} \Big/ \log\left\{1 - \frac{z_0}{x_0}\left(\frac{1}{1+R}\right)\right\}.$$

Naturally, the formula applies generally to the simultaneous nitration of pairs of aromatic substances, provided the assumptions made during its derivation are fulfilled. Even if they are not accurately fulfilled, the general conclusions still hold, for the replacement of k_y/k_x by R, which must in any case represent a too conservative estimate of the ratio of the speeds, leads to the same conclusions. If ω, μ, and π represent the proportions of the individual nitrotoluenes in the total nitrotoluenes produced, the respective coefficients of activation are

$$F_{\text{ortho}} = 3\omega k_y/k_x; \quad F_{\text{meta}} = 3\mu k_y/k_x \; ; \quad F_{\text{para}} = 6\pi k_y/k_x,$$

and on substituting the numerical data, we find

$$F_{\text{ortho}} = 27{\cdot}6 \; ; \quad F_{\text{para}} = 34{\cdot}6; \quad F_{\text{meta}} = 2{\cdot}1.$$

Case 2. *Type* — I. *Examples: Benzyltrimethylammonium Salts and Benzoic Acid.*—The examples mentioned have been chosen to represent this type (which includes all benzene derivatives in which *m*-substitution is known to predominate) because the first corresponds, we consider, with the simple inductive effect, whilst the second theoretically admits of a superimposed electromeric change, and might by some be considered as belonging more properly to one of the categories mentioned in the footnote on p. 2918.

The notoriously slower velocity of many *m*-oriented, as compared with the majority of *op*-oriented, substitutions, taken together with the observations of Martinsen (*loc. cit.*), who has shown, *inter alia*, that the introduction of a carboxyl, sulphonic acid, or nitro-group into a benzene derivative already containing one or more orienting groups diminishes the velocity of further substitution, leaves little doubt that in *m*-substitutions generally the *op*-positions escape an equivalent amount of attack owing to the deactivating influence of the directing substituent. Strictly, the point is unproved, but it is rendered sufficiently probable by the existing evidence to warrant its adoption as a working hypothesis. The question remains as to whether, either generally throughout the category, or in individual

cases, the *m*-position is activated, deactivated, or left unaffected. In certain examples in which a positive pole is attached to the nucleus the answer is clearly that the *m*-position, like the *op*-positions, is deactivated. For the substances mentioned in the head-line, we find that the coefficient of meta-activation is an extremely small fraction of unity, the *o*- and *p*-reactivity factors being smaller still, and we believe that this state of affairs is general amongst *m*-substituting benzene derivatives.

Case 3. *Type* $-\mathrm{I}+\mathrm{T}$. *Examples: The Halogenobenzenes, etc.*—This type includes the halogenobenzenes, the alkyl- and acyl-oxybenzenes, the acyl-, acyl-alkyl, and diacyl-aminobenzenes, nitrosobenzene, phenyl sulphoxides, phenylthionium salts, and all other compounds in which the atom attached to the ring attracts electrons more strongly than hydrogen ($-I$), but at the same time possesses unshared electrons which can be shared with the nucleus ($+T$).

In all the investigated instances, predominating *op*-substitution is the rule; but a substantial amount of simultaneous *m*-substitution is not theoretically impossible, since examples can be conceived in which the inductive process might effectively compete with tautomeric action. In the series of orienting groups NRR′, OR, I, Br, Cl, F (R = alkyl) the tautomeric effect diminishes and the inductive effect increases towards fluorine, but even in fluorobenzene the substitution is almost exclusively ortho-para. On the other hand, the velocity of substitution diminishes throughout the series to such an extent that the right-hand members become qualitatively differentiated from the left-hand members, and from the *op*-orienting groups, belonging to Case 1, which act by simple induction ($+I$). That is to say, the category under consideration provides examples of *op*-orienting groups which, unlike all other *op*-orienting groups, diminish the velocity of substitution: their coefficients of activation are fractional. In this respect they resemble the *m*-orienting groups of Case 2, but are distinguished from them by the fact that for the groups of Case 3 the meta-deactivation is even stronger than the *op*-deactivation, whereas the reverse holds for Case 2. From the left of the above series up to and including iodobenzene the values of k_y/k_x are greater than unity; for bromobenzene (0·2), chlorobenzene (0·01), and fluorobenzene (0·002) they are fractional, and the values given, although approximate, establish the order of the compounds.

The position assigned to the NHAc-group is based on nitration with a neutral reagent in a neutral or feebly acid medium (acetyl nitrate in acetic anhydride; Ingold and Ingold, J., 1926, 1310). The nitration of acetanilide with nitric acid in sulphuric acid as

solvent is interesting inasmuch as the same salt-forming process which absorbs the unshared electrons also charges, and enhances the electron affinity of the nitrogen atom, so that on increasing the strength of sulphuric acid the circumstances of Case 3 continuously approach those of Case 2; this takes place with corresponding changes in the coefficients of activation, which become fractional, and, as Noelting and Collins's experiments indicate, in the proportions of the isomerides (*Ber.*, 1884, **17**, 262).

Case 4. *Type* + I + T. *Example: The Phenoxide Ion.*—The general conditions affecting the substitution of the phenoxide ion are attested by known results. In particular, the high *op*-reactivity of the ion in comparison with undissociated phenol is well illustrated by the recent experiments of Soper and Smith (J., 1926, 1582).

Discussion and Conclusions.—Consideration of the facts summarised above has led us to the following conclusions:

(i) That whereas inductive effects of either sign operate primarily on the ortho- and para-positions, an appreciable second-order effect, always of the same sign as the primary effect, is relayed on to the meta-position.

(ii) That whereas tautomeric effects also operate powerfully on the ortho- and para-positions, no similarly appreciable second-order effect reaches the meta-position.

(iii) That whilst inductive effects give rise to an essentially permanent (not necessarily constant) molecular condition, the tautomeric effect (apart, possibly, from a small permanent residuum) is essentially temporary in character, assuming much greater importance at the moment of attack by a reagent than in the quiescent period preceding it.

Conclusion (i) is reached directly from the consideration of Cases 1 and 2. It implies that *m*-substitution in Case 1 arises from second-order *m*-activation, and in Case 2 from second-order *m*-deactivation, which explains the velocity relations. A consistent deduction is that, as *op*-deactivation increases, the proportion of the effect relayed to the *m*-position decreases, so that the *m*-directive power of a group (Case 2) runs *inversely* as the velocity of *m*-substitution. This is certainly true for a series such as CO_2H(80%), NO_2(93%), $\overset{+}{N}Me_3$(100% meta), in which the velocities rapidly diminish towards $\overset{+}{N}Me_3$ and the figures in brackets represent the proportion of meta-nitration.

Conclusion (ii) follows from Case 3. Considering the series (p. 2922) NRR′, OR, . . ., Cl, F, the term $-I$ may for many purposes be neglected in the left-hand members in comparison with $+T$, which produces strong *op*-activation but no *m*-activation which is

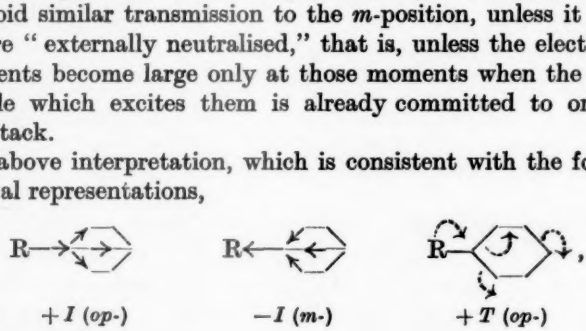
detectable in comparison. Again, if one imagines an extension of the series from NRR′ (*T* strong), through F (*T* weak), towards an extreme representative, such as $\overset{+}{\text{N}}\text{RR′R″}$, of Case 2,

$$\underset{\longleftarrow\ \text{increasing } -I\ \longrightarrow}{\overset{\longleftarrow\ \text{decreasing } T\ \longrightarrow}{\text{NRR′ . . . } (a) \text{ . . . F . . . } (b) \text{ . . . } \overset{+}{\text{N}}\text{RR′R″}}}$$

the change over (*a*) from *op*-activation to *op*-deactivation occurs higher in the series than the change (*b*) from *op*- to *m*-substitution. For groups lying near the first of these critical positions (*a*) in the filled-in series, it is obvious that whilst the tautomeric effect can annul or reverse the strong *op*-deactivation arising from inductive action, it cannot reverse the relatively feeble *m*-deactivation. Indeed it seems to us that the condition of the whole group lying between the critical points (*a*) and (*b*) can be interpreted only along the lines indicated. The application to Case 4 is that appreciable *m*-substitution might arise if the inductive effect (+ *I*) were sufficiently powerful. Arnall's claim (J., 1924, **125**, 811) to have established 2—3% of *m*-substitution in the nitration of phenol might, if confirmed, be an indication in this direction. For systems of groups falling wholly within any one of Cases 1, 3 and 4, *op*-directive power must run parallel with the velocity of *op*-substitution, but no such simple rule can be laid down for the comparison of groups belonging to the different cases.

Conclusion (iii) is tentative, and is introduced because it appears necessary for the reconciliation of conclusions (i) and (ii). That inductive effects give rise to a permanent condition of electronic strain agrees with the known data relating to the molecular dipole moments of benzene derivatives, and it is consistent with our knowledge of reactivity transmission that a fractional part of charges arising on the ortho- and para-carbon atoms should be transmitted to the meta-carbon atom. On the other hand, it is difficult to see how *op*-charges which would be produced by the tautomeric effect can avoid similar transmission to the *m*-position, unless it be that they are "externally neutralised," that is, unless the electron displacements become large only at those moments when the reagent molecule which excites them is already committed to ortho- or para-attack.

The above interpretation, which is consistent with the following graphical representations,



is regarded as partly modifying, and partly giving definition to, the views originally expressed by Ingold and Ingold (*loc. cit.*), and as formulating in a more general way than has hitherto been possible the main principles which underlie the more recent communications from this laboratory on the subject of aromatic substitution. Only benzene substitutions are here dealt with, but the more important applications to naphthalene, quinoline, and certain other simple aromatic systems are sufficiently obvious. It will also be understood that the types discussed grade into one another, and in developing the work we shall investigate ω-halogenated and ω-carboxylated toluenes in order to emphasise this point.

Experimental.

Benzene was purified in the usual way. Toluene was purified by distillation, partial solidification (Ramsay), drying, and re-distillation (b. p. 110·4—110·8°). The other substances mentioned below were purified by distillation or crystallisation.

Toluene (1 mol.) and benzene (1 mol.) were nitrated together in a solution prepared from nitric acid (0·4 mol.) and acetic anhydride, the experiment being otherwise carried out as described by Holleman (*Rec. trav. chim.*, 1914, **33**, 1). Preliminary experiments had shown that for our purpose density determinations made with a moderately large pyknometer provided a more satisfactory method of analysis than measurements of refractive index. Accordingly, pure toluene was nitrated, without benzene, under the conditions indicated, and the mixed mononitro-derivatives were freed from unchanged toluene by distillation until the density remained constant. Mixtures of this product with similarly purified nitrobenzene had the following densities (d) at 25°; p denotes the percentage of nitrobenzene:

p	0·00	1·89	3·66	5·57	9·64	12·05	21·3	100·0
d	1·1526	1·1529	1·1537	1·1551	1·1566	1·1572	1·1616	1·1985

These points all lie on or close to the straight line represented by the equation $d = 1{\cdot}1526 + 0{\cdot}000459p$. The products of the mixed nitrations were likewise distilled to constant density to remove benzene and toluene, and the densities determined. They were d_{25}· 1·1555(i) and 1·1558(ii), which correspond with 6·3%(i) and 6·9%(ii) of nitrobenzene, that is, with 7·0(i) and 7·6(ii) molecules % of nitrobenzene. The agreement being apparently as good as could be expected from the method, the mean value, 7·3 molecules %, which gives $R_{Me} = 12{\cdot}7$, was used to calculate from the formula on p. 2921 that $k_y/k_x = 15{\cdot}7$. From this figure, by means of Holleman's data for the proportions of the isomerides (*loc. cit.*), the coefficients given in the introduction are obtained.

The investigation of the halogenobenzenes was carried out similarly with the following differences: (*a*) 1·0 mol. of nitric acid was used for the preparation of the acetyl nitrate solution, (*b*) the temperature of nitration was 45°, (*c*) the method of analysis was suited to the individual case. The product obtained from the experiments with fluorobenzene was distilled to remove unchanged benzene and fluorobenzene, and the remaining binary mixture hydrolysed with boiling sodium hydroxide solution to remove the fluorine as fluoride ion from the nitrofluorobenzenes—a process which is quantitative. The products obtained from chlorobenzene and bromobenzene were distilled to remove benzene, and the remaining ternary mixtures were hydrolysed under conditions known to be appropriate in each case. The liberated halide ions were estimated, and the residual binary mixtures insoluble in alkali submitted to ultimate analysis. By means of these methods, concordant determinations gave the following values: $R_F = 0{\cdot}0107$, $R_{Cl} = 0{\cdot}027$, $R_{Br} = 0{\cdot}36$, whence the figures given in the introduction were calculated. Competitive nitration of benzene and iodobenzene gave iodonitrobenzenes exclusively (R_I large), and anisole behaved similarly.

Since the medium used in the above experiments does not dissolve benzyltrimethylammonium picrate or benzoic acid sufficiently, a mixture of pure acetic acid and sulphuric acid in equimolecular proportion (15 mols. of each) was used as solvent for the nitration of these substances. The temperature was 0°. In each case, the benzene alone was nitrated and the other substance was recovered pure and unaccompanied by any trace of its nitro-derivatives; this was proved by m. p. and mixed m. p., and, for benzoic acid, confirmed by sublimation. In the course of the nitration of benzyltrimethylammonium picrate, picric acid separated from solution, but we do not regard this as invalidating the experiment, since the benzyltrimethylammonium ion remained dissolved.

The nitration of acetanilide was similarly investigated with identical results.

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CCCLXXXIX.—*Melting Points of the Substituted Amides of Dibasic Acids.*

By CUTHBERT RICHMOND BARNICOAT.

THE members of homologous series usually show a fairly regular variation in physical properties as each series is ascended. The mono- and the di-basic acids are exceptions, as their melting points

rise and fall alternately. Biach (*Z. Physik*, 1904, **50**, 43) pointed out that this alternation is really quite general, as it appears in at least sixteen series of compounds. By plotting the melting points against the number of carbon atoms in the chain, two distinct curves, not necessarily exhibiting rise and fall, are obtained in each case, and those compounds containing an even number of carbon atoms lie on the higher curve. This phenomenon, evident even in the paraffins, appears to be due to something inherent in the carbon chain itself.

Robertson (J., 1908, **93**, 1033; 1919, **115**, 1210) has shown that the amides and substituted amides of the monobasic fatty acids exhibit this irregularity to an even more marked extent than the acids themselves. The investigations did not extend to dibasic acids, and it is to the study of the corresponding compounds of these that this work is confined.

Experimental.

The method of preparation of these substances was much the same as that described in Robertson's papers (*loc. cit.*).

The acids were from Kahlbaum, except the three highest members which were prepared by Lumsden and Walker's method (J., 1901, **79**, 1191).

All the melting-point determinations were made by the capillary-tube method in a castor-oil bath, and are uncorrected. The same standardised thermometer was used throughout.

The compounds not containing bromine were analysed by Kjeldahl's method, and the bromo-derivatives by the chromic acid method (Robertson, J., 1915, **107**, 902).

In Table I are the redetermined values of the melting points of compounds which were already known.

Table I.

Compound.	Formula.	M. p.	Previous observers.
Malonanilide	$C_{15}H_{14}O_2N_2$	224°	225°, 230°
Malono-*o*-toluidide	$C_{17}H_{18}O_2N_2$	189	193
Malono-*p*-toluidide	$C_{17}H_{18}O_2N_2$	247	248, 250
Succinanilide	$C_{16}H_{16}O_2N_2$	227	226
Succino-*p*-toluidide	$C_{18}H_{20}O_2N_2$	260	256
Succino-*o*-toluidide	$C_{18}H_{20}O_2N_2$	231	100 *
Glutaranilide	$C_{17}H_{18}O_2N_2$	223	223, 214
Adipanilide	$C_{18}H_{20}O_2N_2$	235	235, 233, 240
Pimelanilide	$C_{19}H_{22}O_2N_2$	152	155
Suberanilide	$C_{20}H_{24}O_2N_2$	182	183, 187
Subero-*p*-toluidide	$C_{22}H_{28}O_2N_2$	219	218
Azelanilide	$C_{21}H_{26}O_2N_2$	184	185
Sebacanilide	$C_{22}H_{28}O_2N_2$	200	198

* This is probably the melting point of succino-*o*-toluidic acid.

In Table II are the m. p.'s and analyses of the new compounds prepared in connexion with this work.

TABLE II.

Compound.	Formula.	M. p.	% N found.	% N calc.
n-Nonanedicarboxyamide	$C_{11}H_{22}O_2N_2$	173°	12·8	13·1
n-Decanedicarboxyamide	$C_{12}H_{24}O_2N_2$	189	12·0	12·3
n-Nonanedicarboxyanilide	$C_{23}H_{30}O_2N_2$	156	7·45	7·65
n-Decanedicarboxyanilide	$C_{24}H_{32}O_2N_2$	191	7·3	7·4
n-Undecanedicarboxyanilide	$C_{25}H_{34}O_2N_2$	158	7·0	7·1
Glutaro-*o*-toluidide	$C_{19}H_{22}O_2N_2$	222	9·2	9·0
Adipo-*o*-toluidide	$C_{20}H_{24}O_2N_2$	222	8·2	8·6
Pimelo-*o*-toluidide	$C_{21}H_{26}O_2N_2$	174	8·2	8·3
Subero-*o*-toluidide	$C_{22}H_{28}O_2N_2$	185	7·8	7·9
Azelo-*o*-toluidide	$C_{23}H_{30}O_2N_2$	171	7·6	7·65
Sebaco-*o*-toluidide	$C_{24}H_{32}O_2N_2$	179	7·5	7·4
n-Nonanedicarboxy-*o*-toluidide ...	$C_{25}H_{34}O_2N_2$	164	7·0	7·1
n-Decanedicarboxy-*o*-toluidide ...	$C_{26}H_{36}O_2N_2$	164	7·2	6·9
n-Undecanedicarboxy-*o*-toluidide	$C_{27}H_{38}O_2N_2$	142	6·7	6·6
Glutaro-*p*-toluidide	$C_{19}H_{22}O_2N_2$	218	8·7	9·0
Adipo-*p*-toluidide	$C_{20}H_{24}O_2N_2$	241	8·3	8·6
Pimelo-*p*-toluidide	$C_{21}H_{26}O_2N_2$	206	8·2	8·3
Azelo-*p*-toluidide	$C_{23}H_{30}O_2N_2$	198	7·5	7·65
Sebaco-*p*-toluidide	$C_{24}H_{32}O_2N_2$	201	7·2	7·4
n-Nonanedicarboxy-*p*-toluidide ...	$C_{25}H_{34}O_2N_2$	191	7·4	7·1
n-Decanedicarboxy-*p*-toluidide ...	$C_{26}H_{36}O_2N_2$	165	7·0	6·9
n-Undecanedicarboxy-*p*-toluidide	$C_{27}H_{38}O_2N_2$	156	6·5	6·6

In Table III are the m. p.'s and analyses of the new bromo compounds.

TABLE III.

Compound.	Formula.	M. p.	% Br found.	% Br calc.
Succino-*p*-bromoanilide	$C_{16}H_{14}O_2N_2Br_2$	284°	37·4	37·5
Glutaro-*p*-bromoanilide	$C_{17}H_{16}O_2N_2Br_2$	256	36·6	36·4
Adipo-*p*-bromoanilide	$C_{18}H_{18}O_2N_2Br_2$	268	35·5	35·3
Pimelo-*p*-bromoanilide	$C_{19}H_{20}O_2N_2Br_2$	240	34·3	34·1
Subero-*p*-bromoanilide	$C_{20}H_{22}O_2N_2Br_2$	248	33·0	33·2
Azelo-*p*-bromoanilide	$C_{21}H_{24}O_2N_2Br_2$	225	32·1	32·3
Sebaco-*p*-bromoanilide	$C_{22}H_{26}O_2N_2Br_2$	225	31·1	31·4
n-Nonanedicarboxy-*p*-bromoanilide	$C_{23}H_{28}O_2N_2Br_2$	215	30·5	30·5
n-Decanedicarboxy-*p*-bromoanilide ...	$C_{24}H_{30}O_2N_2Br_2$	213	29·5	29·7
n-Undecanedicarboxy-*p*-bromoanilide	$C_{25}H_{32}O_2N_2Br_2$	202	28·9	29·0

Remarks.—Acids. The differences in melting point of adjacent members are considerably greater than those between the corresponding monobasic acids, and the two curves tend to converge. A minimum is obtained at the fifth member (Fig. 1).

Amides. The curves resemble those of the acids, as the terminal groups are somewhat similar. The melting points are on the average 70° higher, and the differences between corresponding members more marked (Fig. 1).

Anilides. The introduction of a phenyl group causes a striking change in the nature of the curves (Fig. 2), that of the odd series

showing greater irregularity than its fellow, and less marked alternation results (*i.e.*, the curves lie closer together). Alternation appears to exhibit an unusual arrangement in fours.

o-*Toluidides* (Fig. 3). There is a marked similarity between these and the two following series, with substituted phenyl groups in the chain. A pronounced maximum is attained at the fifth member. The relative variation between the odd and the even series decreases slightly. The initial irregularity is apparently due to the unsymmetrical arrangement of the *o*-tolyl ring distorting

FIG. 1.

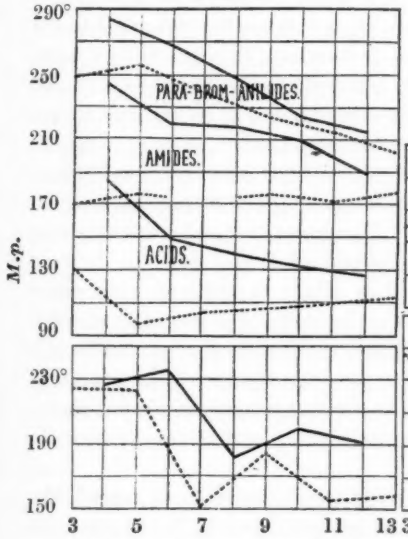

FIG. 2. *Anilides.*

FIG. 3. o-*Toluidides.*

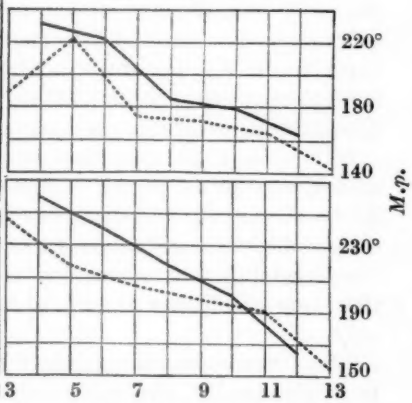

FIG. 4. p-*Toluidides.*

the molecule, particularly when the chain is short and the end groups are in close proximity.

p-*Toluidides* (Fig. 4). The curves show slightly greater variation and the molecule is symmetrical, causing irregularity to be absent.

p-*Bromoanilides* (Fig. 1). The bromine atom has the most marked influence of all the substituents, producing curves almost devoid of irregularity.

I wish to thank Professor P. W. Robertson for his advice and for the interest he has taken in this work.

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CCCXC.—*Aromatic Thionyl and Chlorothionyl Derivatives. Part III. Some Reactions of Thionylalizarin.*

By ALBERT GREEN.

SINCE thionylalizarin appears to be the most reactive of the thionyl compounds previously examined (J., 1924, **125**, 1450; 1926, 2198; this vol., pp. 500, 554, 2341), a further study of its reactions has been carried out.

It is now shown that although the interaction between the thionyl compound and *weak* organic acids provides a general method of preparing the corresponding 2-acyl derivatives of alizarin, yet with the stronger organic acids the thionyl derivative reverts to alizarin. The following acids yield 2-monoacyl derivatives: acetic (*loc. cit.*), phenylacetic, phenoxyacetic, cinnamic, benzoic, *o*-toluic, *m*-bromobenzoic, and *p*-bromobenzoic. Monochloroacetic acid gives a mixture of alizarin and a substance having the appearance of its monochloroacetate, whilst with dichloroacetic, trichloroacetic, and dibromoacetic acids thionylalizarin gives alizarin only.

It is thus clear that the reaction which a thionyl compound undergoes with an organic acid depends on the nature of that acid. The nature of the thionyl compound is also a factor, for while the thionyl derivatives of alizarin and of pyrocatechol are quantitatively converted into their monoacetates (*loc. cit.*) by acetic acid, yet under the same conditions thionylhystazarin (*loc. cit.*) gives hystazarin only.

Diacyl derivatives are obtained by the action of benzoic anhydride, benzoyl chloride and acetyl chloride, but succinic and phthalic anhydrides react neither with thionylalizarin nor with alizarin itself. This may be accounted for by the fact that the production of alizarin succinate (or phthalate) would necessitate the formation of a cyclic structure of eight atoms. Dibenzoylalizarin has been obtained in two crystalline modifications, melting at 160° (labile) and at 187° respectively.

The thionyl compound is rapidly decomposed, with evolution of sulphur dioxide, by boiling absolute ethyl alcohol and by hot phenol and in both cases the products are pure alizarin.

In attempts to prepare ethers by the condensation of thionylalizarin with alkyl halides and with alkyl sulphates no reaction was observed.

Thionylalizarin reacts readily with hot primary aromatic amines, with evolution of sulphur dioxide, to give alizarin, which then undergoes further slow reaction with the bases to yield secondary

amines. For example, in one experiment, the product obtained after boiling thionylalizarin in dry aniline for 1 hour contained less than 1% of nitrogen, gave the reactions of alizarin and melted at 265—268°. This melting point was raised to 275—277° by admixture with pure alizarin. Similar results were obtained with other aromatic amines, and the reaction was not investigated further.

EXPERIMENTAL.

Interaction of Thionylalizarin with Acids, Acid Anhydrides, and Acid Chlorides.—Methods. A. In the case of the lower-melting acids, a slight excess was heated with thionylalizarin at 150—170°. When the evolution of sulphur dioxide was no longer vigorous (usually 10 to 15 minutes), the melt was allowed to cool, boiled with ether to remove any unchanged acid, and the residue was recrystallised from benzene or absolute alcohol. Yields of 90 to 95% of the pure products were obtained.

B. The acid or anhydride and thionylalizarin were heated in dry nitrobenzene at 170° for 40 to 60 minutes. On cooling, a portion of the product usually crystallised. A further quantity was obtained by adding ether to the solution and allowing it to stand. The yields averaged 60%.

C. Benzoyl chloride reacted vigorously at its boiling point with thionylalizarin, and dibenzoylalizarin, m. p. 187°, crystallised on cooling. With acetyl chloride no reaction was observed after 4 hours' boiling, but when the substances were heated in a sealed tube at 150—170° for 2 hours, diacetylalizarin was obtained in 80% yield.

Alizarin benzoates. 2-Monobenzoylalizarin (methods *A* and *B*) was obtained from absolute alcohol in small, chrome-coloured needles, m. p. 208—210° (D.R.-P. 297,261 gives 214—216°). When mixed with a specimen prepared from alizarin and the theoretical amount of benzoyl chloride in pyridine solution, it showed the same m. p. (Found: C, 73·3; H, 3·6. Calc. for $C_{21}H_{12}O_5$: C, 73·3; H, 3·5%).

Dibenzoylalizarin (*B* and *C*). When prepared from the thionyl compound and benzoic anhydride in nitrobenzene solution, *dibenzoylalizarin* separated in clusters of small, pale chrome crystals, m. p. 160°, which was unchanged by further immediate crystallisation from benzene (Found: C, 74·8; H, 3·7. $C_{28}H_{16}O_6$ requires C, 75·0; H, 3·6%). This labile form, on being kept for a week in contact with a little of the original nitrobenzene solution, was transformed to the stable modification, which consisted of stout, primrose prisms, m. p. 187° (Found: C, 74·9; H, 3·7%) (compare Barnett and Cook, J., 1922, **121**, 1389). Other preparations of this derivative from

alizarin and benzoyl chloride in pyridine gave the higher-melting form.

The following 2-*monoacyl* derivatives of alizarin were also prepared. The methods of preparation are indicated, and the calculated values for C, H, and Br are given in brackets after the found values.

2-Acyl derivatives of alizarin.	Appearance and m. p.	Recrystallisation solvent and analyses.
Phenylacetyl (*A*) ...	Greenish-yellow needles, m. p. 165°.	Benzene. 73·7; 4·0 (73·7; 3·9).
Phenoxyacetyl (*A*) ...	Small, yellow needles, m. p. 179°.	Benzene. 70·7; 3·7 (70·6; 3·7).
Cinnamoyl (*A* and *B*)	Golden-yellow prisms, m. p. 209°.	Benzene. 74·5; 3·7 (74·6; 3·8).
o-*Toluoyl* (*A*)	Fine, ochre needles, m. p. 192°.	Benzene or absolute alcohol. 73·7; 3·9 (73·7; 3·9).
m-*Bromobenzoyl* (*A*)	Small, greenish-yellow needles, m. p. 214°.	Toluene. Br, 18·7 (18·9).
p-*Bromobenzoyl* (*B*)	Greenish-yellow needles, m. p. 195°.	Benzene. Br, 18·9 (18·9).

Condensations with Halogen-substituted Acetic Acids.—(1) *Monochloroacetic acid.* Thionylalizarin (2 g.) was treated with the carefully purified acid, according to method *A*. The product, crystallised from benzene, consisted of 1·6 g. of an intimate mixture of fine, yellow needles, which closely resembled the monoacyl compounds previously examined, and of fine, reddish-brown flakes. The mixture contained 5·8% of chlorine (the monochloroacetate requires 11·2%). Similar results were obtained by varying the experimental conditions. After repeated extraction of the mixtures with light petroleum, a residue of pure alizarin was obtained; m. p. 288°, either alone or mixed with an authentic specimen.

(2) Thoroughly dried and purified dichloro-, trichloro-, and dibromo-acetic acids in all experiments gave theoretical yields of halogen-free alizarin, which was identified by mixed melting-point determinations with the pure substance, and by conversion into the diacetate.

The products from alcoholic and phenolic solutions of thionylalizarin were shown to be alizarin in the same manner.

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THE EDWARD DAVIES LABORATORIES, UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH. [*Received, September 3rd*, 1927.]

CCCXCI.—*The Isomerism of the Oximes. Part XXXII. Sulphates.*

By Oscar L. Brady and Alan D. Whitehead.

Luxmoore (J., 1896, **69**, 180) showed that α-benzaldoxime could be converted into the β-isomeride by means of concentrated sulphuric acid and isolated both the α- and the β-benzaldoxime sulphate, $C_6H_5{\cdot}CH{:}NOH,H_2SO_4$. The α-oxime sulphate regenerated the α-oxime on decomposition with aqueous ammonia at 0°, and on keeping rapidly changed to the β-oxime sulphate; this gave the β-oxime on treatment with alkalis. A number of other aromatic aldoxime sulphates have now been prepared and Luxmoore's method of converting the α- into the β-oxime has been investigated in the hope that it would prove more convenient than the usual procedure through the hydrochloride. Further, it was thought that it might be possible, through the sulphate, to bring about isomeric change in those oximes which do not form hydrochlorides (Brady and Dunn, J., 1915, **107**, 1862; Brady and Manjunath, J., 1924, **125**, 1068).

When α- *o*-, *m*-, or *p*-nitro- or α-*p*-methoxy-benzaldoxime is dissolved in concentrated sulphuric acid, the sulphate of the α-oxime is first formed, and the solution on neutralisation with sodium carbonate regenerates the α-oxime; if the solution be kept for some time or heated to 100°, or if the temperature rises too much during the dissolution owing to the heat of reaction, the sulphate of the β-oxime is produced, and the solution on neutralisation gives the β-oxime. Provided that the temperature is kept low, the dry sulphates of these oximes, isolated by various means from the freshly prepared solutions, consist mainly of the α-form, differing in this respect from the hydrochlorides, since, although the α-hydrochloride of *p*-methoxybenzaldoxime can be obtained at — 10°, those of *m*- and *p*-nitrobenzaldoxime are stable only at very low temperatures (Brady and Dunn, J., 1916, **109**, 680; 1923, **123**, 1798). The solid sulphate from benzaldoxime consisted of the β-form (compare Luxmoore, *loc. cit.*). In the case of α-*o*-methoxybenzaldoxime, which cannot be converted into the β-isomeride through the hydrochloride, sulphate formation likewise failed to bring about the change; α-*o*-chlorobenzaldoxime, which yields the β-form only with difficulty through the hydrochloride, gave only an α-sulphate; 3 : 4-methylenedioxybenzaldoxime gave an α-sulphate which could not be converted into the β-form owing to decomposition of the methylene group on heating or keeping. α-6-Nitro-3 : 4-methylenedioxybenzaldoxime and α-6-bromo-3 : 4-dimethoxybenzaldoxime,

which do not form hydrochlorides, gave α-sulphates, but these compounds did not change to the β-forms.

When solutions of α-benzaldoxime, *o*-, *m*-, and *p*-nitro-, and *p*-methoxy-benzaldoximes in concentrated sulphuric acid were heated for a short time at 100°, cooled, and poured into a large excess of sodium carbonate solution, products were obtained which on crystallisation gave fairly satisfactory yields of the β-oximes. This method is probably the quickest way of preparing small amounts of the β-oximes, but does not work well with quantities much above 2 grams; it seems that owing to the longer time required for neutralisation when larger quantities are used, as in the case of the hydrochlorides, partial reversion of the β- to the α-oxime takes place.

Prolonged heating of aldoximes with concentrated sulphuric acid results in the formation of the corresponding amides. It is impossible to decide at present whether this is a Beckmann change (I) or dehydration to nitrile followed by addition of water in another way (II), since the nitrile on similar treatment yields the amide.

$$\mathrm{R{\cdot}\overset{|}{C}O{-}NH_2} \longleftarrow \underset{(\mathrm{I.})}{\mathrm{R{\cdot}\overset{\|}{C}{\cdot}OH{-}HN}} \longleftarrow \mathrm{R{\cdot}\overset{\|}{C}H{-}HO{\cdot}N} \longrightarrow \underset{(\mathrm{II.})}{\mathrm{RCN}} \longrightarrow \mathrm{R{\cdot}CO{\cdot}NH_2}$$

o-Nitro-, *o*-methoxy-, 3 : 4-methylenedioxy-, and 6-nitro-3 : 4-methylenedioxy-benzaldoxime undergo extensive charring on heating with sulphuric acid and could not be investigated under such conditions.

Experimental.

α-Benzaldoxime.—Formation of β-oxime. The method of converting the α- into the β-oxime by means of sulphuric acid has been investigated in order to find the best conditions. When benzaldoxime was dissolved in 96% sulphuric acid (5 g.) the temperature rose to 40—50° and after 4·5 g. of oxime had been added the solution became thick with crystals of benzaldoxime sulphate. If the solid sulphate was separated from the acid, pressed on a porous tile, and added to excess of 2*N*-sodium carbonate, fairly pure β-oxime was obtained, but when the whole semi-solid material was slowly stirred into a volume of 2*N*-sodium carbonate containing 4 mols. of carbonate for each mol. of acid used (this will subsequently be referred to as neutralisation), an oil separated consisting of a mixture of β- and unchanged α-oxime. With 5 g. of oxime and 10 g. of acid, complete solution was attained, but neutralisation gave a waxy product still containing much α-oxime. When a solution of 5 g. of oxime in 20 g. of acid was kept for a month in a closed flask, or when a

solution of 1 g. of oxime in 5 g. of acid was heated on the water-bath for 30 minutes, the product obtained yielded on neutralisation a fairly pure β-oxime (m. p. 108—111°), one crystallisation from benzene giving the pure compound.

Formation of benzamide. A solution of α-benzaldoxime (5 g.) in concentrated sulphuric acid (15 g.) was heated on the water-bath for 12 hours, kept for 2 days, and neutralised, a white precipitate being obtained. The suspension was extracted with ether and then with chloroform. The ethereal solution contained impure β-benzaldoxime (identified by comparison with an authentic specimen and by conversion into the α-benzoyl derivative; the yield was 14% of the oxime taken), no aldehyde or nitrile, and 1·42 g. of benzamide; 1 g. of benzamide was obtained from the chloroform extract, the total yield being approximately 50% of the oxime taken. The aqueous solution, after being acidified with hydrochloric acid, yielded to ether 0·6 g. of benzoic acid, corresponding to 12% of the oxime employed. Of the 24% of the oxime unaccounted for, most was probably lost during manipulation, some possibly as sulphonate.

α-m-*Nitrobenzaldoxime.*—When the oxime (1 g.) was stirred into sulphuric acid (2 g.), the temperature rose to 35°. The almost colourless, viscous solution was cooled in a desiccator for 30 minutes and poured into dry ether. The precipitated α-m-*nitrobenzaldoxime sulphate* was collected, washed rapidly twice with dry ether, and kept for 12 hours in an evacuated desiccator. It consisted of a white, crystalline powder, m. p. 71—76°, and was analysed by decomposition of a weighed amount with water and titration of the sulphuric acid with *N*/10-sodium carbonate and methyl-orange (Found: H_2SO_4, 41·2. $C_7H_6O_3N_2,H_2SO_4$ requires H_2SO_4, 37·1%). The freshly prepared solid sulphate on decomposition with 2*N*-sodium carbonate regenerated the α-oxime.

When α-*m*-nitrobenzaldoxime (2 g.) was dissolved in sulphuric acid (10 g.), and the solution neutralised at once, a product, m. p. 107°, was obtained which was almost pure α-oxime. If the solution was kept for 24 hours before being neutralised, the recovered oxime melted at 75°, indicating that about 50% conversion had occurred; whilst if the solution was heated on the water-bath for 30 minutes and then neutralised, a fairly pure β-oxime was obtained which gave a good yield of pure β-*m*-nitrobenzaldoxime after one crystallisation from benzene.

α-*m*-Nitrobenzaldoxime (5 g.) was dissolved in sulphuric acid (15 g.) and heated for 7 hours on the water-bath. On neutralisation of the clear brown solution an oil separated which soon solidified.

The whole was extracted once with ether, the undissolved solid was collected and dissolved in hot chloroform, and the aqueous layer also was extracted with chloroform. The ethereal solution was extracted twice with 2*N*-sodium hydroxide, and then with a solution of hydroxylamine hydrochloride in excess of 2*N*-sodium hydroxide to remove aldehyde as the sodium salt of the oxime; the aqueous layer in the latter case was but faintly coloured, indicating that little aldehyde was present. The ether on evaporation yielded 0·8 g. of somewhat impure *m*-nitrobenzamide, one crystallisation from water giving the pure product. The sodium hydroxide extracts were saturated with carbon dioxide and the precipitated oxime was extracted with ether, 2·1 g. of a mixture of α- and β-oximes being obtained (the time of manipulation would account for some conversion of β- into α-oxime); crystallisation from water, containing a little hydrochloric acid to convert the β- into the α-oxime, yielded pure α-*m*-nitrobenzaldoxime. The combined chloroform solutions were extracted with 2*N*-sodium hydroxide and the faintly coloured alkaline solution was added to those obtained from the ethereal extract. The chloroform on evaporation gave 0·5 g. of *m*-nitrobenzamide.

m-Nitrobenzonitrile (2 g.) was heated with sulphuric acid (6 g.) for 7 hours; some charring occurred due probably to the presence of a little of the *o*-nitro-compound. On neutralisation a dark solid was precipitated which, after crystallisation from water (animal charcoal), gave more than 1 g. of pure *m*-nitrobenzamide.

m-Nitrobenzamide often crystallises with water of crystallisation and must be kept in a desiccator for 12 hours before its melting point is taken. A specimen, crystallised from hot water with rapid cooling and dried rapidly by pressing on several porous tiles, collapsed in a melting-point tube when this was put into a bath at 105°, but it did not melt until 141°. On being kept in a desiccator, it lost 12·4% of its weight (calc. for $1H_2O$, 9·8%); the high result is due to the difficulty of freeing the compound from extraneous moisture.

The following sulphates were prepared by analogous methods, and the products of their decomposition investigated as before. The results are described in the introduction. The compounds consist, unless otherwise stated, of white microcrystalline powders. α-o-*Methoxybenzaldoxime sulphate* (1 g. of oxime; 4 g. of acid), m. p. 143° (Found: H_2SO_4, 38·3. $C_8H_9O_2N,H_2SO_4$ requires H_2SO_4, 39·3%). α-o-*Chlorobenzaldoxime sulphate* (1 g. of oxime; 1 g. of acid) (Found: H_2SO_4, 36·9. C_7H_6ONCl,H_2SO_4 requires H_2SO_4, 38·6%). α-6-*Bromo*-3 : 4-*dimethoxybenzaldoxime sulphate* (1 g. of

oxime; 2 g. of acid), a canary-yellow, granular solid, m. p. 105° (Found: H_2SO_4, 27·7. $C_9H_{10}O_3NBr,H_2SO_4$ requires H_2SO_4, 27·3%). α-6-*Nitro*-3 : 4-*methylenedioxybenzaldoxime sulphate* (1 g. of oxime; 1 g. of acid), a brown powder, m. p. 110—135°, readily dissociating into oxime and acid in the presence of ether or on exposure to moist air (Found: H_2SO_4, 31·1. $C_8H_6O_5N_2,H_2SO_4$ requires H_2SO_4, 31·8%). p-*Nitrobenzaldoxime sulphate*, a light fawn, granular solid too deliquescent for a melting point to be obtained (Found: H_2SO_4, 38·6. $C_7H_6O_3N_2,H_2SO_4$ requires H_2SO_4, 37·1%). This compound dissociates very easily and is difficult to obtain; it was prepared by adding the oxime (1·5 g.) to sulphuric acid (1 g.) until the mixture began to crystallise; the pasty mass was stirred into ether, rapidly collected, and washed once only with dry ether. No solid sulphate could be obtained from *o*-nitrobenzaldoxime, only a very small amount of oil being precipitated from the sulphuric acid solution by ether. α-3 : 4-*Methylenedioxybenzaldoxime sulphate* (Found: H_2SO_4, 37·6. $C_8H_7O_3N,H_2SO_4$ requires H_2SO_4, 37·2%) was obtained by stirring the oxime (2·5 g.) into acid (2 g.) warmed to 60°, cooling, collecting the solid which separated, and washing it with dry ether. α-p-*Methoxybenzaldoxime sulphate* (2 g. of oxime; 10 g. of acid), m. p. 79—80° (Found: H_2SO_4, 38·9. $C_8H_9O_2N,H_2SO_4$ requires H_2SO_4, 39·3%).

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CCCXCII.—*Properties of Conjugated Compounds. Part III. The Bearing of Hexatriene Chemistry on the Reactive Form of Conjugated Hydrocarbons.*

By ERNEST HAROLD FARMER, BANARSI DAS LAROIA, THEODORE MACLEAN SWITZ, and JOCELYN FIELD THORPE.

THE chemistry of hexatriene is of fundamental importance from two standpoints. First, although a simple conjugated hydrocarbon, its additive behaviour is at variance, according to van Romburgh's observation, with the requirements of the Thiele hypothesis, and secondly its structure allows the anticipation of two geometrical isomerides, one of which, approaching so closely the Kekulé representation of benzene, has been a subject of speculation in respect of a possible valency connexion between the terminal carbon atoms.

With van Romburgh's hexatriene the evidence for 3 : 4-addition

is, apparently, convincing. The formation of the hydrocarbon from Griner's *s*-divinylglycol (I) (the reduction product of acraldehyde, *Ann. Chim. Phys.*, 1892, **26**, 368) through the 3 : 4-dibromide (II)

$\begin{matrix}\mathrm{CH(OH)\cdot CH{:}CH_2}\\ \mathrm{CH(OH)\cdot CH{:}CH_2}\end{matrix}$	$\begin{matrix}\mathrm{CHBr\cdot CH{:}CH_2}\\ \mathrm{CHBr\cdot CH{:}CH_2}\end{matrix}$	$\begin{matrix}\mathrm{CH\cdot CH{:}CHPh}\\ \mathrm{CH\cdot CH{:}CHPh}\end{matrix}$
(I.)	(II.)	(III.)

would appear quite normal; further the crystalline product obtained by adding bromine to the hydrocarbon, since it is identical with the parent dibromide (II), would be naturally regarded as a 3 : 4-dibromide. At the outset of this investigation this series of reactions appeared to offer an attractive method for testing the generality of the 3 : 4-additive mode in the hexatriene series. Thus it was found with a 1 : 6-diphenylhexatriene (III) synthesised from cinnamaldehyde through stages analogous to (I) and (II), that out of the very numerous geometrical, stereo-, and position isomerides theoretically possible the additive dibromide actually obtained was identical with the parent dibromide; with 1 : 6-dimethylhexatriene and 2 : 5-dimethyl-1 : 6-diethylhexatriene, which were also synthesised, polymerisation took place too rapidly to allow of satisfactory bromination.

Derivation of Hexatriene Bromides.

Re-examination of the *s*-divinylglycol from acraldehyde showed that, contrary to Griner's opinion, it was a mixture of *meso* and *racemic* forms: on reduction, it yielded two forms of *s*-diethylglycol, each oxidisable to propionic acid. On replacement of hydroxyl by bromine with phosphorus tribromide under Griner's conditions—conditions under which much hydrogen bromide was liberated—the product, so far from being homogeneous, consisted of solid and liquid bromides boiling over a considerable range. Excluding the highest-boiling fraction consisting of a tribromohexene (the formation of which was reduced to a minimum by modifying Griner's method), the material consisted of a liquid and a solid, designated for convenience (A) and (B). Of these, the solid (B) was the compound utilised by van Romburgh for generating hexatriene, whilst (A), an impure liquid dibromide, undoubtedly suffered progressive conversion into the isomeride (B), the active agent in the conversion being in all probability the hydrogen bromide liberated during distillation. Although in purifying this unstable substance repeated fractionation involving considerable loss of material was necessary, large quantities of it were prepared. On treatment with zinc it yielded a new hydrocarbon closely approach-

ing van Romburgh's compound in physical properties and superficially indistinguishable therefrom. Whereas the new hydrocarbon yielded an oily dibromide (C) (by far the most stable of the liquid dibromohexadienes encountered) and on further bromination an oily tetrabromide, the dibromide and tetrabromides (two) from van Romburgh's hydrocarbon were all crystalline.

To this second hydrocarbon, differing entirely in its additive bromides from dihydrobenzene, must be attributed the hexatriene structure, the only feasible relationship with the known hexatriene being one of *cis-trans* isomerism as in (IV) and (V).

(IV.) $CH_2{:}CH{\cdot}CH$ ‖ $HC{\cdot}CH{:}CH_2$ $\qquad$ $HC{\cdot}CH{:}CH_2$ ‖ $HC{\cdot}CH{:}CH_2$ (V.)

The different chemical behaviour of these substances was discovered at a very early stage, but trustworthy evidence as to which was the *trans-* and which the *cis*-form was difficult to secure. A series of oxidations undertaken in the hope of retaining the $\gamma\delta$-carbon atoms in recognisable products such as maleic or tartaric acid proved fruitless. Attention was therefore centred on the dibromides (A), (B), and (C), structural discrimination between which represented the only apparent approach towards the elucidation of hexatriene chemistry. Of hexatriene dibromides which demand consideration, there are, excluding improbable 1 : 3-, 2 : 4-, and 2 : 5-forms, seven structures (geometrical, stereo-, and position isomerides) theoretically derivable from *trans*-hexatriene and an additional one from *cis*-hexatriene. Here again in the assignation of formulæ, direct oxidation methods had to be abandoned; some thirty oxidations of the various dibromides with different reagents were carried out and, except in one important particular mentioned later, yielded little useful information.

Structural Relationship of Hexatriene Dibromides.

Griner had observed that the solid dibromide (B) gave a diethoxyhexadiene with alcoholic potash. This conversion was found to be almost quantitative when sodium ethoxide was used, and the homogeneous product had the advantage, unusual in this series, of considerable stability. On catalytic hydrogenation it yielded diethoxyhexane, which was successively convertible by usual processes into di-iodohexane, dicyanohexane, and a dibasic acid. The last proved to be suberic acid, indicating that the substituents at each stage occupied the 1 : 6-positions. Evidence as to the position of the double bonds in diethoxyhexadiene was obtained by

ozonisation : the ozonide yielded with water γ-ethoxycrotonaldehyde, ethoxyacetaldehyde, and the corresponding acids.

$$\mathrm{EtO{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OEt} \longrightarrow \begin{matrix} \mathrm{EtO{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CHO} & + & \mathrm{EtO{\cdot}CH_2{\cdot}CHO} \\ \downarrow & & \downarrow \\ \mathrm{EtO{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CO_2H} & & \mathrm{EtO{\cdot}CH_2{\cdot}CO_2H} \end{matrix}$$

The constitution of the parent dibromide follows from that of its diethoxy-derivative. It is true that change of substituent position during the transformation with sodium ethoxide is not entirely out of the question, but this possibility is discounted by several considerations. Not only was there no positive indication of such change, but degradation of the ozonide of the dibromide repeatedly failed to yield any recognisable trace of formaldehyde or of formic acid ; the high boiling point of the dibromide compared with those of its isomerides was also in keeping with the 1 : 6-constitution. Thus a 3 : 4-glycol yields a 1 : 6-dibromide and the hydrocarbon derived from the latter adds bromine terminally.

Evidence bearing on the change from 3 : 4-glycol to 1 : 6-dibromide was furnished by the parent dibromide of the new hexatriene. This lost hydrogen bromide with such facility that the corresponding diacetate, diethoxy-compound, and glycol were unobtainable from it : it yielded a hydrocarbon, C_6H_6, of strong acetylenic odour and a bromohexatriene—a mode of reaction pointing to the constitution (VI).

$$\underset{\text{(VI.)}}{\mathrm{CH_2{:}CH{\cdot}CHBr{\cdot}CHBr{\cdot}CH{:}CH_2}} \xrightarrow[\mathrm{NaOH}]{\text{alc.}} \begin{cases} \mathrm{CH_2{:}CH{\cdot}CH{:}CBr{\cdot}CH{:}CH_2} \\ \mathrm{CH_2{:}CH{\cdot}C{:}C{\cdot}CH{:}CH_2} \end{cases}$$

This constitution is, moreover, the only one which permits of debromination without necessitating general valency rearrangement. As such rearrangement would lead in all probability to a *trans*-form, the new hydrocarbon, which has the slightly lower boiling point, is regarded as a *cis*-form.

Whether or no the 3 : 4-dibromide (A) consists essentially of one stereoisomeric form is uncertain. The preferential disappearance

$$\begin{matrix} & \mathrm{CH_2{:}CH{\cdot}CH(OH){\cdot}CHBr{\cdot}CH{:}CH_2} & \longrightarrow & \mathrm{CH_2{:}CH{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}CH_2Br} \\ (a) & \uparrow & & \downarrow \\ & \text{Glycol} & & \text{1 : 6-dibromide} \\ & \downarrow & & \uparrow \\ (b) & \text{3 : 4-dibromide} & \longrightarrow & \text{1 : 4-dibromide} \end{matrix}$$

of one stereoisomeric configuration in the change 3 : 4-glycol ⟶ 3 : 4-dibromide ⟶ 1 : 6-dibromide is conceivable, but there are

indications that to some extent the change proceeds as in scheme (*a*). Of the alternative scheme (*b*), which involves complete bromination before isomerisation, it may be said that efforts directed towards detecting the presence of the intermediate 1 : 4-dibromide gave no positive result. The yield of hydrocarbon repeatedly obtained from (A) (30%) was consistent with the presence of a proportion of less readily debrominated dibromide but was equal to that of van Romburgh's hydrocarbon from the homogeneous form (B).

Migration of Bromine.

The formation of the 1 : 6-dibromide from the 3 : 4-glycol has every appearance of involving the migration of bromine. If of common occurrence, the existence of such a facility is a consideration of the utmost importance in arriving at a *generalised* representation of the reactive form of conjugated hydrocarbons. The phenomenon is already known in the saturated hydrocarbon series (Lucas and Jameson, *J. Amer. Chem. Soc.*, 1924, **46**, 2476) and there is accumulating a considerable body of evidence that bromine migration in unsaturated hydrocarbons happens frequently; further, the general tendency of such halogen movement appears to be towards the assumption of terminal position with respect to a previously conjugated unit. Illuminating instances are those of hydrogen bromide addition to isoprene and $\beta\gamma$-dimethylbutadiene (Claisen, *J. pr. Chem.*, 1922, **105**, 68; Bergmann, *J. Russ. Phys. Chem. Soc.*, 1920, **52**, 37). In both cases, the first-formed tertiary bromide arising by 1 : 2-addition isomerises to a primary bromide, apparently the result of terminal addition; both changes are unexplainable by hydrogen migration. The question as to the primary or secondary nature of an additive product is vital, and if facile change from a primary to a secondary product is prevalent where bromine is the addendum, it is also to be suspected, speaking of hydrocarbons, where hydrogen is the addendum; in the latter case, however, proof is exceedingly difficult for obvious reasons.

The number of well-authenticated instances of 1 : 4-addition to hydrocarbons is very small. The production of a 1 : 4-dibromide from isoprene has recently been established (Bergmann, *loc. cit.*, p. 24; Staudinger, *Helv. Chim. Acta*, 1922, **5**, 756); the formation of a considerable proportion of the 1 : 2-dibromide of butadiene along with the 1 : 4-product is recorded by Straus as a private communication from Thiele (*Ber.*, 1909, **42**, 2872), and the formation of a 1 : 4-dibromide of *cyclo*pentadiene is recorded by Thiele (*Annalen*, 1900, **314**, 296). The behaviour of butadiene, isoprene, and *cyclo*pentadiene is at present being further examined, but in 1909 Straus (*loc. cit.*) expressed the opinion that whilst 1 : 4-addition

may occur, it is not the rule. He went beyond this in stating that no case was then known, at least among open-chain compounds, where 1 : 4-addition took place exclusively. Straus's further reflexion concerning the gloomy prospect afforded by the necessity of exhaustively determining the constitution of each single additive product before judging the position of entering halogen atoms suggests either a specific additive mode for each substance, or rather (since the reactive form of the addendum, molecular or atomic, is regarded as a possible contributing feature) that the joint relation of unsaturated hydrocarbon and addendum is specific. Leaving out of consideration the reactive form of the addendum, the formation of two or more additive dibromides for any conjugated hydrocarbon may be viewed in two ways : either the latter has two or more distinct tendencies towards reaction, possibly expressible by an equilibrium between reactive forms (compare Chandrasena and Ingold, J., 1922, **121**, 1312), or one or more of the products arise by secondary process—in the latter case the isomeric change is in no wise dependent on the reactive form of the parent hydrocarbon. For an equilibrium between the reactive forms of hydrocarbons there is no direct experimental evidence (compare Farmer and Healey, this vol., p. 1060).

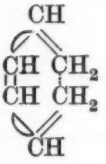
Yet van Romburgh's hexatriene adds bromine terminally. Obviously, if the foregoing considerations hold good, the 1 : 6-product may be no less a secondary product than the same compound is when formed from a 3 : 4-glycol. Since free hydrogen bromide and possibly free bromine are promoters of migratory changes, the use of a brominating agent other than commercial bromine is indicated in striving to isolate the primary additive bromide. Gupta and Thorpe (J., 1922, **121**, 1896) have investigated the employment of dibromodimethyldihydroresorcinol as a source of bromine in substitution reactions, and Rosenmund and Kuhnhenn (*Ber.*, 1923, **56**, 1262) have used the hydrobromide of quinoline dibromide with success in both substitution and additive reactions. When the quinoline derivative is employed with van Romburgh's hexatriene, instead of complete transformation into the solid dibromide, the latter (B) is replaced to a large extent (usually about 65%) by a new liquid dibromide (D), which is comparatively stable at room temperature but is converted (with slight decomposition and evolution of a little hydrogen bromide) into the

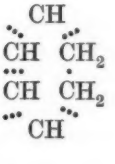
(VII.) $CH_2{:}CH{\cdot}\overset{\|}{C}H$
 $HC{\cdot}CHBr{\cdot}CH_2Br$ $\qquad$ $CH_2{:}CH{\cdot}\overset{\|}{C}H$
 $HC{\cdot}CH{:}CHBr$ (VIII.)

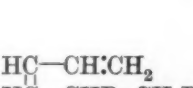
1 : 6-form (B) on distillation. The only reasonable formula for this substance (D) is (VII), a constitution borne out by its behaviour

with alcoholic alkali. With this reagent, as anticipated, (D) did not yield an acetylenic hydrocarbon, nor did it yield a diethoxy-derivative—a circumstance rendering a *cis-cis-* or *cis-trans*-1 : 6-configuration highly improbable—but conversion into a bromohexatriene readily took place. The further characterisation of the dibromide (VII) and its derivative (probably VIII) was not possible with the material at disposal.

Turning to *cis*-hexatriene, residual valency or electronic formulæ such as (IX) and (X) automatically disappear with the denial of an activated form in which the three unsaturated centres of the chain are fused.

(IX.) 

(X.) 

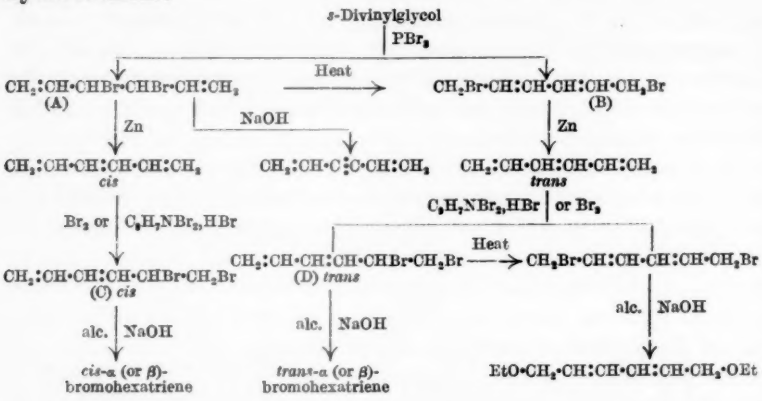


(XI.)

But whether the reactive form of the hydrocarbon is an open-chain or pseudo-cyclic structure, the formation of a 1 : 6-dibromide would be expected to result in the appearance of the solid (B), since the necessary valency adjustment consequent on addition should lead to the assumption of the *trans-trans*-configuration no less than in the case of addition to *trans*-hexatriene. Both hexatrienes being regarded as open-chain forms, then of those additive modes which would tend to destroy differentiation between the respective additive products there are 1 : 6 (compelling valency reorganisation), 3 : 4 (removing the double bond which is the seat of geometrical isomerism) and 1 : 4 (compelling valency reorganisation). Neglecting 1 : 3-, 3 : 5-, etc., forms, there is left only the 1 : 2-form, so that the only distinction between the 1 : 2- dibromides from the two hydrocarbons should be one of spatial distribution as in (VII) and (XI).

It was found by experiment that the dibromide (C) from the new hexatriene behaved in quite different fashion from the known 1 : 6- and 3 : 4-forms. It was not convertible into an acetylenic hydrocarbon or a diethoxy-derivative, but, like the labile product (D) from van Romburgh's hexatriene, readily yielded with alkali a bromohexatriene. The great difference between the forms (C) and (D) is the tendency towards bromine migration in the latter contrasting with the high degree of stability of the former. This difference is quite compatible with the widely different steric conditions in the two compounds and it is noteworthy that the dibromide (C) obtained by using commercial bromine appeared in every

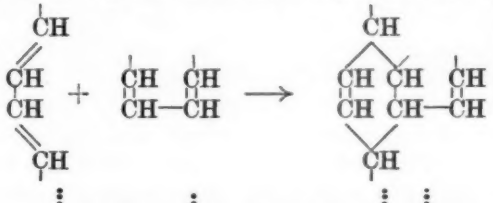
respect identical with that obtained by using quinoline dibromide hydrobromide.



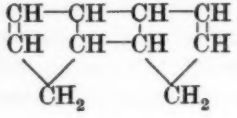
The halogen atoms of certain of the additive dibromides of this series possess marked lability : *e.g.*, the dibromide of 1 : 6-diphenylhexatriene reverts to the hydrocarbon on treatment with diethylamine or pyridine, whilst the dibromides (A) and (B) readily liberate iodine from potassium iodide acidified with acetic acid. This lability, which has not as yet been extensively examined, varies considerably with the nature, and possibly the spatial distribution, of the groups R, R′ in the complex R·CHBr·R′. For instance, whilst diphenylhexatriene dibromide loses its bromine with pyridine as noted above, the solid hexatriene dibromide (B) yields a stable pyridinium salt of type PyBr–CH_2·CH:CH·CH:CH·CH_2–PyBr and analogous compounds with diethylamine and aniline. Evidence on the subject of bromine migration is furnished by Prévost in two papers which escaped the authors' notice until a late stage in the investigation. It is shown (*Compt. rend.*, 1926, **183**, 1292) that erythrol, CH_2:CH·CH(OH)·CH_2·OH, when treated with phosphorus tribromide in pyridine solution, yields not the expected 1 : 2-dibromo-Δ^3-butene, but 1 : 4-dibromo-Δ^2-butene, CH_2Br·CH:CH·CH_2Br. Thus the transformation already known to take place when the hydroxyl groups of substituted vinylcarbinols are replaced by bromine, R·CH(OH)·CH:CH_2 $\xrightarrow{PBr_3}$ R·CH:CH·CH_2Br, is repeated with vinylglycol (erythrol). Consequently the suspicion arose that *s*-divinylglycol might behave similarly, and this author enumerates (*Compt. rend.*, 1927, **184**, 458) certain observations of Griner (*loc. cit.*) that are inconsistent with a 3 : 4-constitution for solid hexatriene dibromide. In support of this view, he succeeded in obtaining from the latter a glycol and the corresponding diacetate which differed in properties from *s*-divinylglycol and its diacetate;

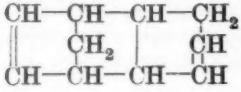
moreover, the molecular exaltations of these two derivatives are consistent with the constitutions $HO\cdot CH_2\cdot CH{:}CH\cdot CH{:}CH\cdot CH_2\cdot OH$ and $AcO\cdot CH_2\cdot CH{:}CH\cdot CH{:}CH\cdot CH_2\cdot OAc$ respectively.

The chemistry of hexatriene is intelligible on the basis of bromine migration in a non-conjugated system, but although it is clear that a terminal additive product is by no means the necessary outcome of primary additive reaction, and although it may be demonstrable that a terminal product may arise merely by isomerisation of a different additive form, there is as yet no certainty that it may not also arise as a primary product of addition. Thus whilst there can be no other conclusion than that the attempts which have been made from time to time (compare Allsop and Kenner, J., 1923, **123**, 2296) to retain the Thiele hypothesis by restricting its scope to conjugated hydrocarbons cannot stand when bromine and hydrogen bromide are the addenda considered, it is possible that the modern extension of the Thiele hypothesis which allows of two or more types of polarisation, one or more of which may come into play as determined by the nature and reactive condition of the addendum, may cover the experimental observations. At the same time, the extent to which addition to an unsaturated compound may be considered as determined by unsaturated compound and addendum separately is by no means clear. In this respect polymerisation processes are of great interest. If butadienoid compounds in general polymerise in the manner suggested by Lebedef (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1249) it would seem



that the forms $\cdot CH{:}CH\cdot CH{:}\dot{C}H$ and $CH{:}CH\cdot\dot{C}H{:}CH$ (or their electronic equivalents) may co-exist and that additive mode is determined by the reactive state of each particular addendum. The usual co-existence of such forms would account for the difference between the recorded tendencies towards polymerisation of open-chain butadienes and *cyclo*pentadiene, the latter yielding under the exigencies of spatial configuration a dimeride (XII) (Staudinger, *Helv. Chim. Acta*, 1924, **7**, 23) rather than (XIII).

(XII.) 



(XIII.)

Nevertheless the appearance of ready isomerisation among the products of addition to conjugated hydrocarbons is a factor demanding consideration in estimating the significance of current reaction formulæ. It is hoped shortly to submit further evidence on the subject of *primary* additive products.

Experimental.

s-*Divinylglycol.*

Reduction.—The glycol (prepared in large quantities from the pure stabilised acraldehyde of Messrs. Poulenc Frères by the method of Griner, *loc. cit.*) was reduced at atmospheric pressure and room temperature with palladium and hydrogen. Absorption was rapid and somewhat exceeded the requirements of simple hydrogenation —a fact explained by the formation of some quantity of a volatile alcohol, presumably ethylpropylcarbinol. On working up the product in the usual way, a liquid was obtained; one portion of this (b. p. 87—89°/15 mm.) remained almost completely liquid at —20°, whilst the remainder (b. p. 89—91°/15 mm.) solidified in the receiver of the apparatus. The former, after being freed as far as possible from the latter and redistilled, was obtained as a colourless, mobile oil, b. p. 87—88°/15 mm. (Found: C, 60·6; H, 11·8. $C_6H_{14}O_2$ requires C, 61·0; H, 11·9%). The latter crystallised from light petroleum in white plates, m. p. 88° (Found: C, 60·5; H, 11·8%). Both substances gave good yields of propionic acid (identified as the anilide, m. p. 105°) when carefully oxidised with dilute potassium permanganate. They must therefore be stereoisomeric forms of s-*diethylethylene glycol.*

Bromination.—Numerous methods of halogenation were tested. The most satisfactory reagent was phosphorus tribromide. Griner's procedure (*loc. cit.*, p. 380) was followed, but it was found advantageous to employ a mechanical stirrer and extract the product (after pouring on ice) with ether. The well-washed extract was dried and the main bulk of solvent removed on a steam-bath. The remaining ether was removed at reduced pressure, and the residual oil diluted with light petroleum and cooled in a freezing mixture. The crystals of dibromide (B) (m. p. 85°) which separated were removed and the procedure of cooling and filtering twice was repeated. The ultimate filtrate was freed from solvent as above, and the residual oil fractionated. To avoid gross decomposition, it was necessary to distil the crude liquid, first, at 1 mm. pressure; subsequently three fractions were collected, (*a*) a small portion boiling below 80°/11 mm., (*b*) b. p. 80—115°/11 mm., (*c*) b. p. 115—140°/11 mm. The portion (*b*), on redistillation, passed over

almost entirely at 80—95°/10 mm.; this material corresponded in composition approximately with hexatriene dibromide, but contained a material which caused considerable carbonisation on standing for a few hours. To obtain some idea of the correct boiling point of the pure dibromide, the sub-fractions indicated were analysed ($C_6H_8Br_2$ requires C, 30·0; H, 3·4; Br, 66·6%).

	Percentage composition.		
B. p.	C.	H.	Br.
80—87°/10 mm.	32·2	4·4	63·4
88—92°/11 mm.	31·0	4·1	—
90—95°/10 mm.	31·1	3·9	65·0
90—96°/11 mm.	30·0	4·0	64·7

Finally, a considerable quantity of a pale yellow oil (A), b. p. 94—96°/11 mm., was obtained, which was used in subsequent operations (Found: C, 30·0; H, 3·6; Br, 66·6%). This substance could not be kept for many days at room temperature owing to the rapidity of carbonisation.

The higher-boiling material, after separation by the above-described method of a quantity of solid dibromide which commenced to crystallise on cooling, consisted mainly of a yellow oil, b. p. 135—140°/11 mm. This was evidently a *tribromohexene* (Found: Br, 73·1. $C_6H_9Br_3$ requires Br, 74·8%). It was subsequently found that the proportion of this substance was greatly reduced when bromination was effected by gradually pouring a chloroform solution of the glycol into a chloroform solution of phosphorus tribromide. With this procedure, however, it was particularly necessary to avoid undue heating of the crude mixture of bromides whilst removing the solvent.

Dibromide (A) *and its Derivatives.*

γδ-Dibromo-Δ$^{\alpha\epsilon}$-hexadiene.—All attempts to demonstrate the constitution of the dibromide (A) by direct oxidation failed. The assigned formula rests upon the properties of the substance in relation to those of the three isomeric dibromides.

(a) *Isomeric Change.*—It was repeatedly observed during distillation of this liquid that a portion of the material suffered change of boiling point. This was not very marked at pressures of 1—4 mm., degradation (accompanied by liberation of hydrogen bromide) then being slight, but was much more marked at pressures of 10—22 mm., degradation being appreciable. From the higher-boiling portions so produced, crystals of the solid dibromide invariably separated. The loss of material sustained in this way was considerable and in conjunction with the initial low yield of crude bromides rendered

the accumulation of adequate quantities of reasonably pure liquid dibromide very laborious.

(b) *Ease of Hydrogen Bromide Removal.*—Numerous attempts were made to prepare the glycol and the diacetate of the glycol corresponding to this dibromide. In every case, owing to the loss of hydrogen bromide, the product was a mixture of substances of very different boiling point from which no pure substance could be fractionated. With alcoholic sodium ethoxide, loss of hydrogen bromide was still more complete : a $\gamma\delta$-diethoxyhexadiene was therefore unobtainable.

For rapid removal of hydrogen bromide alcoholic sodium hydroxide was found to be the best reagent. Sodium ($1\frac{1}{2}$ atoms) was dissolved in aqueous alcohol, and the cold solution added gradually, with shaking, to an alcoholic solution of the dibromide (1 mol.). The separation of sodium bromide was completed by heating the mixture for a few minutes on a steam-bath, after which the product was cooled and poured into water. An oil was precipitated : this was well washed with water, dried with calcium chloride, and fractionated. Two fractions were collected, (*a*) b. p. 80—95° and (*b*) b. p. 50—60°/22 mm. Redistillation of the former yielded a colourless, mobile hydrocarbon of penetrating, acetylenic odour. The ease with which this substance, doubtless $\Delta^{\alpha\epsilon}$-*hexadien-γ-in*, polymerised rendered purification and analysis very difficult, and a detailed study of its properties impossible (Found : C, 91·1 ; H, 7·2. C_6H_6 requires C, 92·3 ; H, 7·7%). The fraction (*b*) yielded a faintly yellow liquid, b. p. 52—55°/20 mm., which could not be completely freed from the polymeric products of the hydrocarbon. This substance, which polymerised completely in 24 hours, resembled, in its very characteristic odour, the bromohexatrienes later described. There can be little doubt that it was *γ-bromohexatriene* (Found : Br, 49·3. C_6H_7Br requires Br, 50·3%).

(c) *Bromine Addition.*—The dibromide, dissolved in chloroform, absorbed bromine readily at first, but later absorption was slow. After removal of the solvent at reduced pressure and distillation, the tetrabromide (presumably $\alpha\beta\gamma\delta$-*tetrabromo*-Δ^{ϵ}-*hexene*) was obtained as a yellow oil (b. p. 155—158°/11 mm.) which remained liquid at − 25° (Found : Br, 79·7. $C_6H_8Br_4$ requires Br, 80·0%).

cis-Hexatriene.—To 3 : 4-dibromohexadiene, dissolved in 5 times its bulk of 98% alcohol, excess of zinc dust was added in small amounts, the reaction mixture being finally heated for 20 minutes on a steam-bath. The zinc residue was filtered off and the filtrate poured into several times its bulk of water. The oily layer was separated and washed ten times with small quantities of water. Subsequent drying over calcium chloride and distillation yielded a

colourless liquid (b. p. 75—83°) and a considerable quantity of high-boiling material. On redistillation the former boiled at 78·5°/760 mm. Yield 30%. This hydrocarbon resembled van Romburgh's hexatriene in odour and in proneness to polymerisation; the latter property in conjunction with high volatility rendered analysis difficult. The density and molecular exaltation ($d_4^{20°}$ 0·7175; $n_D^{20°}$ 1·4577; $[R_L]_D$ 30·41) are lower than the latest values recorded by van Romburgh for the isomeric hydrocarbon (Found: C, 88·5; H, 11·6. C_6H_8 requires C, 90·0; H, 10·0%). It is probable that the new hydrocarbon contained van Romburgh's hexatriene to the extent of 2—2½%.

Dibromide (C) *and its Derivatives.*

cis-αβ-*Dibromo-*$\Delta^{\gamma\epsilon}$*-hexadiene.*—Bromine (2 atoms) was added to a chloroform solution of *cis*-hexatriene kept below 0°. Addition was very rapid. The product, after removal of the solvent at reduced pressure, was a colourless oil (all the other dibromides were yellow in liquid form), b. p. 90—96°/11 mm. (Found: Br, 66·5. $C_6H_8Br_2$ requires Br, 66·6%). There was a very small residue of the solid dibromide (B), representing about 1½—2½% of the hexatriene employed.

A colourless, stable dibromide quite indistinguishable from the above was obtained by employing quinoline dibromide hydrobromide in place of free bromine (method of Rosenmund and Kuhnhenn, *loc. cit.*). The acetic acid solution of the product was poured into ice-water, and the oily dibromide extracted with ether. It was necessary to remove the usual small amount of solid dibromide (B) before distillation.

The corresponding tetrabromide (tetrabromohexene) was obtained by employing 4 atoms of bromine instead of 2 atoms. It consisted of a large proportion of a yellow oil, b. p. 155—158°/11 mm. (Found: Br, 79·8. $C_6H_8Br_4$ requires Br, 80·0%), and a very small proportion of a solid which crystallised from petroleum in colourless needles, m. p. 91° (Found: C, 18·1; H, 2·7; Br, 79·6. $C_6H_8Br_4$ requires C, 18·0; H, 2·0; Br, 80·0%).

cis-α(or β)-*Bromohexatriene.*—The dibromide (C) (1 mol.) was dissolved in a little alcohol and to it an alcoholic solution of sodium ethoxide (2 mols.) was added drop by drop with shaking. The reaction was completed by heating the mixture for ½ hour on a steam-bath. On cooling and pouring the mixture into water an oil was precipitated. This was extracted with ether and dried, and the solvent removed under a column. The residue, which contained no volatile hydrocarbon, was distilled. An almost colourless liquid possessing the characteristic bromohexatriene odour passed

over at 45—65°/20 mm., leaving much material, apparently the product of extensive polymerisation. On redistillation, the bulk of the distillate boiled at 52—55°/20 mm. (Found : Br, 48·5. C_6H_7Br requires Br, 50·3%). This substance polymerised extensively in 24 hours.

Dibromide (B) *and its Derivatives.*

αζ-Dibromo-Δ$^{\beta\delta}$-hexadiene.—Numerous attempts were made to demonstrate the constitution of Griner's solid dibromide (m. p. 85°) directly. As these had little success, the constitution of its diethoxy-derivative (below) was fully examined, the possibility of isomerisation during conversion being discounted by many observations.

The two forms of the corresponding tetrabromide (possibly *αβεζ-tetrabromo-Δ$^{\gamma}$-hexene*) are incorrectly described by Griner (*loc. cit.*, p. 383). The less soluble isomeride, after successively crystallising from chloroform and light petroleum, yielded colourless prisms, m. p. 111° (Found : Br, 80·0. Calc. : Br, 80·0%); the more soluble separated from light petroleum in colourless prisms, m. p. 46° (Found : Br, 80·3%). These tetrabromides showed very great stability towards oxidation by ozone and by permanganate.

Behaviour with Organic Bases.—When a dry ethereal solution of pyridine (2 mols.) was added to a dry solution of the solid dibromide (B) a bulky precipitate separated. This substance, which was readily soluble in water, appeared to be quite free from pyridine hydrobromide. It crystallised from alcohol–ether in colourless plates, m. p. 212°, and appeared to be the *dipyridinium* salt, $PyBr{-}CH_2{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH_2{-}PyBr$ (Found : Br, 41·2. $C_{16}H_{18}N_2Br_2$ requires Br, 40·2%). Analogous compounds were formed with aniline and diethylamine, but were not further investigated. Dry distillation of the dipyridinium compound yielded a large amount of pyridine dibromide and a minute quantity of a liquid with a garlic-like odour.

αζ-Diacetoxy-Δ$^{\beta\delta}$-hexadiene.—A mixture of the dibromide (50 g.) with glacial acetic acid (50 g.) was added to excess of potassium acetate moistened with glacial acetic acid (50 g.). The whole was heated on a steam-bath for 24 hours. The cooled mass was poured into water, and the product isolated in the usual way. As it still contained bromine, it was heated for a further period with potassium acetate and acetic acid. Finally a product almost free from bromine was obtained. The bulk of this distilled at 155—160°/14 mm. as a colourless oil (Found : C, 60·8; H, 7·0. $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·1%).

αζ-Diethoxy-Δ$^{\beta\delta}$-hexadiene.—The solid dibromide (B) was added to the requisite quantity of thoroughly cooled alcoholic sodium

ethoxide. The product was well shaken and gradually heated till ebullition set in. The reaction was completed by heating for ¾ hour on a steam-bath. After cooling, the reaction mixture was poured into water, and the precipitated oil extracted with ether. The diethoxy-compound was obtained in almost quantitative yield as a colourless, mobile oil (b. p. 116°/20 mm.) of characteristic odour (Found: C, 70·5; H, 10·8. Calc.: C, 70·6; H, 10·6%). This corresponds to Griner's product (regarded as γδ-diethoxy-$\Delta^{\alpha\epsilon}$-hexadiene) obtained by the action of alcoholic potash on the same dibromide (*loc. cit.*, p. 388).

Reduction of αζ-Diethoxy-$\Delta^{\beta\delta}$*-hexadiene.*—Diethoxyhexadiene (10 g.) was reduced with colloidal palladium and hydrogen at room temperature and atmospheric pressure. Reduction was rather slow at the beginning but became rapid later and was complete in about 3½ hours. The amount of hydrogen absorbed was about 35% in excess of that theoretically required for reducing two double bonds. On pouring the reaction mixture into water and working up in the usual way the product was found to consist of two substances, (*a*) a colourless liquid of strong odour (b. p. 38—45°/14 mm.), appreciably volatile in ether vapour and very volatile in alcohol vapour, and (*b*) a less volatile, colourless liquid (b. p. 80—90°/14 mm.). The former (about 5 g.), which was almost certainly *α-ethoxyhexane*, distilled completely at 42°/14 mm., but was not quite free from the second product (Found: C, 72·2; H, 13·0. $C_8H_{18}O$ requires C, 73·8; H, 13·8%); the latter (about 3 g.), which possessed a faint odour and distilled at 86°/14 mm., was *αζ-diethoxyhexane* (Found: C, 70·2; H, 12·5. $C_{10}H_{22}O_2$ requires C, 70·0; H, 12·6%).

αζ-Di-iodohexane.—Diethoxyhexane contained in a Carius tube was saturated with dry hydrogen iodide, the weight of gas absorbed being noted. The tube was sealed and heated at 100° for 16 hours. It was then cooled, opened, and re-treated with hydrogen iodide until the requisite quantity of this gas (2 mols.) had been absorbed. It was again heated for 16 hours. The cooled product consisted of a small, colourless layer which seemed to be mainly alcohol (free from any considerable amount of ethyl iodide) and a heavy, dark brown layer. The latter was dissolved in ether, washed with sodium bicarbonate solution and water, and dried with calcium chloride. This crude di-iodohexane, which was only slightly deficient in iodine, was converted into the corresponding dinitrile without further purification.

αζ-Dicyanohexane.—The crude di-iodohexane was converted into the dinitrile with potassium cyanide as described by Hamonet (*Compt. rend.*, 1903, **136**, 244). The dinitrile was isolated by pouring the reaction product into water and extraction with ether. The

dried extract gave a good yield of a pale yellow oil, which differed from the di-iodide in its ready solubility in alcohol.

Suberic acid. When heated with concentrated hydrochloric acid for 1 hour, the crude dinitrile was hydrolysed and gave an excellent yield of suberic acid, which separated from water in colourless needles, m. p. 138°, mixed m. p. 138° [Found : C, 55·2; H, 7·9; *M* (dibasic), 177. Calc. : C, 55·2; H, 8·0%; *M*, 174].

Oxidation of αζ-Diethoxy-Δ$^{\beta\delta}$-hexadiene.—A stream of ozonised oxygen was passed for 14 hours through a chloroform solution of this substance. The solvent was then removed at reduced pressure. The colourless, syrupy ozonide was shaken with 50 c.c. of water, and the mixture warmed until complete decomposition took place (85°). The yellow aldehydic oil was separated from the aqueous layer and dissolved in ether. From the ethereal extract, freed from acidic matter by shaking it several times with dilute bicarbonate solution, and dried with calcium chloride, the aldehyde was obtained as a mobile, pungent-smelling oil; from the alkaline washings a yellow syrupy acid was extracted by ether. This gave an aldehydic reaction, but deposited, on long standing in a vacuum desiccator, a few crystals (long, colourless prisms, m. p. 45°) of a non-aldehydic acid. The combination of melting point, equivalent (micro-titration, 135), unsaturated nature, and its ready solubility in water and petroleum suggested that the latter acid was γ-ethoxycrotonic acid (compare Lespieau, *Compt. rend.*, 1905, **140**, 723). This was subsequently confirmed (below).

The residual syrupy acid was fractionated. The bulk distilled at 106—107°/21 mm. as a colourless, mobile liquid. Since the basicity of this substance was nearly that of ethoxyacetic acid (the degradation product complementary to γ-ethoxycrotonaldehyde), it was converted into the *p*-bromophenacyl ester. An excellent yield of *p*-bromophenacyl ethoxyacetate was obtained therefrom by the method of Judefind and Reid (*J. Amer. Chem. Soc.*, 1920, **42**, 1047) : this crystallised in colourless plates, m. p. 104·5°, and agreed in properties with the product described by these authors (Found : C, 48·1; H, 4·4. Calc. : C, 47·8; H, 4·3%).

The aldehydic oil was separated into four fractions by distillation, (*a*) below 75°/21 mm., (*b*) 75—85°/21 mm., (*c*) 85—100°/21 mm., and (*d*) a viscous residue which partly distilled on strong heating to yield a colourless, mobile oil which polymerised to a jelly on standing for several days. Of these fractions, (*b*) and (*c*) constituted the bulk of material. The former, which distilled almost completely at 80°/21 mm., did not yield a semicarbazone or phenylhydrazone but corresponded in composition with *γ-ethoxycrotonaldehyde* (Found : C, 62·8; H, 8·9. $C_6H_{10}O_2$ requires C, 63·1; H, 8·8%). This

constitution was confirmed by oxidation (below). From fraction (*a*) a small quantity of impure ethoxyacetaldehyde (b. p. 70°) was isolated. As this was insufficient for adequate fractionation, it was oxidised to ethoxyacetic acid (below).

Oxidation of γ-Ethoxycrotonaldehyde and Ethoxyacetaldehyde.—These oxidations were conducted in almost exactly the way described by Delépine and Bonnet (*Compt. rend.*, 1909, **149**, 39). The former yielded a solid acid which crystallised from light petroleum in colourless prisms, m. p. 45°. This acid was γ-ethoxycrotonic acid [Found: C, 55·2; H, 7·6; *M* (monobasic), 133. Calc.: C, 55·4; H, 7·7%; *M*, 130] and was identical with that formed directly during the decomposition of the ozonide.

The oxidation product of ethoxyacetaldehyde was a liquid. This was identified as ethoxyacetic acid by conversion into the *p*-bromophenacyl ester described above.

trans-*Hexatriene.*—Van Romburgh's hydrocarbon, regarded as *trans*-hexatriene, was prepared from the dibromide (B) as described for the *cis*-compound.

As observed by van Romburgh, when a chloroform solution of bromine (1 mol.) was added to a chloroform solution of the hydrocarbon (1 mol.) at 0°, conversion into the solid dibromide (αζ-dibromo-$\Delta^{\beta\delta}$-hexadiene) was complete.

Dibromide (D) *and its Derivatives.*

trans-αβ-*Dibromo-*$\Delta^{\gamma\epsilon}$*-hexadiene.*—When quinoline dibromide hydrobromide (1 mol.) was gradually added at 0° to a well-agitated solution of the *trans*-hydrocarbon in glacial acetic acid, bromination was readily effected. The product was poured into ice-water, and the oily suspension filtered. After removal of a quantity of the solid bromide (B) by filtration the filtrate was extracted with ether. The extract was washed until free from acetic acid and dried, and the ether was evaporated, finally under reduced pressure. The oily residue was dissolved in light petroleum and cooled to −25°; the solid dibromide which separated was filtered off and the cooling and filtering repeated. After removal of the bulk of the solvent by gentle heating and of the remainder under reduced pressure, a yellow oil was obtained (yield, 65%) (Found: Br, 65·2. $C_6H_8Br_2$ requires Br, 66·6%). A small quantity of this distilled under 1—2 mm. pressure without apparent decomposition. When cautious distillation of a larger portion at 22 mm. pressure was attempted, the distillation of the first few drops (b. p. 107°/21 mm.) was concurrent with a rapid darkening in colour and a slight evolution of hydrogen bromide. Isomeric change had taken place, for further distillation occurred only at a much higher temperature.

On cooling, the contents of the flask, which had previously remained liquid at — 25°, set to a solid mass of the dibromide (B). The extent of conversion of the liquid to the solid dibromide was very high.

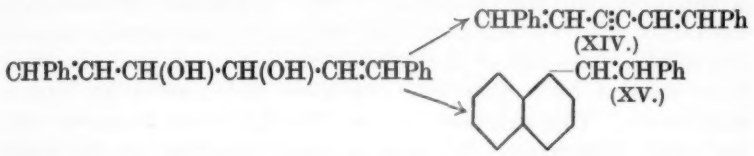
trans-α(or β)-*Bromohexatriene.*—Removal of hydrogen bromide from the liquid *trans*-αβ-dibromohexadiene (above) was effected precisely as with the corresponding *cis*-compound (p. 2949). Much polymerisation appeared to have occurred during the reaction, for only a portion of the product was distillable. A faintly yellow liquid, b. p. 53°/22 mm., was obtained which possessed the characteristic odour of bromohexatriene (Found : Br, 48·2. C_6H_7Br requires Br, 50·3%). This substance polymerised the most rapidly of the three isomerides : within 15 minutes of distillation a scaly deposit appeared on the sides of the vessel and within 2 hours the change was complete.

Derivatives of αζ-Diphenylhexatriene.

s-*Distyrylethylene Glycol* (*Hydrocinnamoin*).—Reduction of cinnamaldehyde was effected by Thiele's method (*Ber.*, 1899, **32**, 1296). Separation of the solid glycol from the viscous oil was best effected by completely dissolving the latter in hot alcohol and cooling the solution in a freezing mixture. The crystals so obtained, when washed with a little ether and recrystallised once from alcohol, attained at once the correct melting point (153—154°). Yield 10—12%.

The residual viscous oil was treated with steam to remove volatile matter, cooled, dissolved in ether and dried over sodium sulphate. Removal of the solvent left a transparent jelly, which was kept in an evacuated desiccator for a week. Portions of the substance were examined in the following manner to ascertain whether it contained isomeric distyrylglycols or their corresponding hydrocarbons : (a) *Distillation.* About half the material distilled between 110° and 200° at 3 mm. ; the remainder was undistillable (solid distyrylethylene glycol distils readily at 2 mm.). The portion, b. p. 130—200°/3 mm., deposited colourless plates, m. p. 206°, which dissolved in ether and benzene to give fluorescent (bluish) solutions. This hydrocarbon had previously been noted by Thiele (*loc. cit.*), and his view that it may be phenyl-α-naphthylethylene appears to be correct : the substance is unimolecular in benzene solution, and of the dehydration products (XIV) and (XV) the latter accounts for our inability to effect any reduction with hydrogen and colloidal palladium (Found : C, 93·9 ; H, 5·5 ; *M*, cryoscopic, 225. Calc. : C, 93·9 ; H, 6·0% ; *M*, 230). (b) *Dehydration.* When the material was heated with acetic anhydride for 4 hours at 150°, two substances were obtained, the hydrocarbon (XV) and an oil (more mobile than

the original one) from which no definite product could be isolated. (c) *Attempted benzoylation.* Treatment with benzoyl chloride



(Schotten–Baumann conditions) yielded again the hydrocarbon (XV). (d) *Bromination.* Addition of bromine yielded no identifiable product, but phosphorus tribromide gave a small quantity of the diphenyldibromohexadiene, m. p. 124°, described below, and other non-purifiable products.

Dibromo-αζ-diphenylhexadiene.—To phosphorus tribromide (20—25 g.), dissolved in dry ether at 0°, distyrylethylene glycol (5 g.) was added in small amounts, with vigorous shaking. The temperature was allowed to rise during addition and the product was kept at room temperature for ¾ hour. The mass was poured on ice and the pale yellow solid which was precipitated was filtered off and washed with ether. The filtrate was extracted with ether, and the extract thoroughly washed and dried. The bulk of the solvent was evaporated and the remainder removed under reduced pressure. The residue was a yellow, sticky mass which was freed from oil by washing with ether. The united solid portions were dried and recrystallised from petroleum, yielding colourless crystals (3·5 g.) of *dibromo-αζ-diphenylhexadiene*, m. p. 124—125° (Found: Br, 41·0. $C_{18}H_{16}Br_2$ requires Br, 40·8%). The ethereal washings yielded a small amount of a yellow oil, which was very unstable and rapidly caused the decomposition of the solid dibromide if left in contact with it. This substance was probably also a dibromide; mixtures of the two when treated with zinc yielded only the diphenylhexatriene described below.

αζ-Diphenylhexatriene.—To the dibromide, m. p. 124—125°, dissolved in 50 c.c. of chloroform, zinc dust (1 g.) was added in small portions with thorough shaking. The mixture was then warmed for ½ hour on a steam-bath. The cooled product, diluted with much ether, was washed with dilute sulphuric acid and water, and dried. On concentration and cooling, a crop of shining, yellow leaflets (m. p. 196°) separated. This hydrocarbon, which was crystallisable from chloroform, was undoubtedly the same diphenylhexatriene obtained by Smedley (J., 1908, **93**, 376) through condensing sodium phenyl*iso*crotonate with cinnamaldehyde in presence of acetic anhydride (Found: C, 94·0; H, 6·6. Calc.: C, 93·1; H, 6·9%). Yield 60—65%.

Bromination of αζ-Diphenylhexatriene.—Addition of bromine (1 mol.) to the hydrocarbon (1 mol.) dissolved in a large bulk of carbon disulphide was effected at — 20°. When absorption, which was rather slow, was complete, the product was thoroughly washed and dried. Removal of the solvent yielded a solid which, after being washed with ether, was colourless and needed no further purification. This substance, m. p. 124—125°, was identical with the solid dibromide (dibromo-αζ-diphenylhexadiene) from which the hydrocarbon had been prepared. When thus obtained, it was quite free from the traces of impurities which promoted decomposition (Found : Br, 40·7%).

The *tetrabromide* and *hexabromide* were formed with increasing difficulty by further addition of bromine. The former crystallised in white prisms, m. p. 165° (Found : Br, 58·7. $C_{18}H_{16}Br_4$ requires Br, 57·9%), and the latter in stout needles, m. p. 228—230° (Found : Br, 67·8. $C_{18}H_{16}Br_6$ requires Br, 67·4%).

Action of Organic Bases on Diphenylhexatriene Dibromide.—Diethylamine (1 g.) was added to the dibromide (1 g.) dissolved in absolute ether. In 2 days a heavy precipitation (about 1 mol.) of pearly-white diethylamine hydrobromide, m. p. 212°, had taken place. This salt was removed and the ethereal solution was washed with dilute acid and with water and dried. On concentration, it deposited a considerable amount of pure diphenylhexatriene, m. p. 196°.

Pyridine also gave, under similar conditions, the same hydrocarbon.

Derivatives of αζ-Dimethylhexatriene [$\Delta^{\beta\delta\zeta}$-*Octatriene*].

s-*Dipropenylethylene Glycol.*—Crotonaldehyde was reduced in analogous manner to acraldehyde (compare Charon, *Ann. Chim. Phys.*, 1899, **17**, 266). The glycol, a faintly yellow oil, b. p. 120—122°/9 mm., was obtained in 50—60% yield.

Bromination of s-*Dipropenylethylene Glycol.*—The method which gave the best results is the following. The glycol (50 g.), dissolved in dry ether, was added drop by drop to a solution of phosphorus tribromide (200 g.) in dry ether (100 c.c.). At first the temperature was kept below 10°; later, occasional moderation by cooling kept it in the neighbourhood of room temperature. When addition was complete, the mixture was kept for ¾ hour and then poured on ice. After careful washing and drying, the major portion of the solvent was distilled from a steam-bath and the remainder at reduced pressure. No solid bromide was isolable and complete carbonisation of the crude liquid was avoided only by distillation at greatly reduced pressure, all access of air to the hot liquid being prevented.

At 1 mm. a large proportion distilled: this distillate yielded fractions 68—85°/14 mm., 85—100°/14 mm., and 100—120°/14 mm., all of which had nearly the correct bromine content. The substance obviously contained two or more isomeric dibromides along with small amounts of impurity which promoted rapid decomposition at room temperature. As adequate separation of the isomerides was impossible by fractionation, the above fractions were united and redistilled; a portion, b. p. 92—100°/14 mm., was utilised for subsequent experiments. This was an almost colourless liquid which darkened in a few hours and became almost black in 24 hours (Found: Br, 56·3. $C_8H_{12}Br_2$ requires Br, 59·7%).

αζ-Dimethylhexatriene.—The dibromide (30 g.) yielded with zinc and alcohol (see p. 2948) an oil, much of which distilled between 45° and 112° at 25 mm. Only the portion, b. p. 45—55°/25 mm., was bromine-free: this was redistilled at ordinary pressure and a fraction, b. p. 120—130°, was collected. Thus about 8 c.c. of a somewhat impure, colourless hydrocarbon of distinctive odour were obtained (Found: C, 84·8; H, 11·2. C_8H_{12} requires C, 89·9; H, 11·1%). This, on further fractionation through a small column, yielded 2 c.c. of hydrocarbon, b. p. 125—130° (Found: C, 87·7; H, 11·4%; $d_4^{18°}$ 0·8394; $n_D^{18°}$ 1·45193; $[R_L]_D$ 34·70). Numerous attempts to obtain purer and larger specimens of the hydrocarbon were made. The rapidity of polymeric and oxidative changes, however, caused great loss both during the debromination process and subsequently; soft, wax-like flakes rapidly appeared on the walls of the vessel containing the hydrocarbon and in a few hours the latter changed into a jelly.

βε-Dimethyl-αζ-diethylhexatriene [*δη-Dimethyl-Δ$^{\gamma\eta}$-decatriene*].

α-Methyl-β-ethylacraldehyde was prepared from propaldehyde by Döbner and Weissenborn's method (*Ber.*, 1902, **35**, 1144).

δη-Dimethyl-Δ$^{\gamma\eta}$-decadiene-εζ-diol.—Methylethylacraldehyde was reduced in similar fashion to acraldehyde. The *glycol* was a rather viscous, yellow oil, b. p. 163—165°/23 mm. It was soluble in water and the common organic solvents and did not solidify at — 25° (Found: C, 72·8; H, 11·3; $d_4^{19°}$ 0·9400; $[R_L]_D$ 59·20. $C_{12}H_{22}O_2$ requires C, 72·7; H, 11·1%).

εζ-Dibromo-δη-dimethyl-Δ$^{\gamma\eta}$-decadiene.—The glycol (20 g.) was added in drops to an ethereal solution of phosphorus tribromide (100 g.). After 1 hour, the mixture was poured on ice, and the dibromide extracted with ether. The dried ethereal solution yielded, on evaporation, a white, sticky mass: this was taken up in light petroleum and warmed with animal charcoal. After filtration, white

prisms, m. p. 99—100°, separated (Found: Br, 50·2. $C_{12}H_{20}Br_2$ requires Br, 49·4%).

βε-*Dimethyl-αζ-diethylhexatriene.*—By the action of zinc on dibromodimethyldecadiene (in alcoholic solution) a product of variable boiling point was obtained. Since even the lowest-boiling fraction still contained bromine, the whole was re-treated with zinc. Much polymeric change attended these operations, waxy scales separating on the sides of the containing vessel. A quantity of unsaturated hydrocarbon of strong odour (colourless liquid, b. p. 65—70°/26 mm.) was obtained, but this still contained traces of bromine and polymerised too rapidly to allow of adequate fractionation. The obvious impurity of this specimen (Found: C, 76·0; H, 11·2. $C_{12}H_{20}$ requires C, 87·8; H, 12·2%) rendered it unsuitable for further use.

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CCCXCIII.—*The Reactions between Oxygen and Coal.*

By WILFRID FRANCIS and RICHARD VERNON WHEELER.

A STUDY of the gases occluded in coal that had been exposed to the air for a long time (see Wheeler, J., 1918, **113**, 945) suggested that one reaction between oxygen and coal, or some part of the coal substance, was analogous to that between oxygen and carbon which results in the formation of a physico-chemical complex (Rhead and Wheeler, J., 1913, **193**, 461). Later work (Tideswell and Wheeler, J., 1919, **115**, 895; 1920, **117**, 794) emphasised the analogy by showing that, not only did exhaustion of coal at a slightly higher temperature than that at which "fixation" of oxygen had taken place remove part of the oxygen as oxides of carbon, but also that the coal then had a renewed capacity for attaching oxygen. To explain this "revivification," it was assumed that the molecular structure of that part of coal to which oxygen attaches itself approximated to that of carbon.

We have recently shown (J., 1925, **127**, 112, 2238; 1926, 1410) that the portion of coal most readily attacked by oxygen at low

temperatures is the ulmin portion, the molecular structure of which contains a compact system of 5- and 6-membered rings, which recalls the compact 6-membered ring structure suggested for carbon by Aschan (*Chem.-Ztg.*, 1909, **33**, 561). The analogy between the oxidation of carbon and that of coal is not, however, complete. During the latter, the hydrogen-containing groupings of the ulmin molecule play an important part, whilst stable acidic (carboxylic) groupings are formed which have no counterpart in the composition of the carbon–oxygen complex formed when carbon is oxidised.

In the present research, which should be considered in conjunction with that of Tideswell and Wheeler (*loc. cit.*), whose methods of experiment we have followed, we have studied more particularly the behaviour of the hydrogen-containing groupings of the ulmin molecule during the oxidation of coal, as disclosed by the formation of water. Oxygen was circulated at a constant rate through powdered coal maintained at a constant temperature, and periodic measurements were made of the total quantity of oxygen disappearing and of the quantities of each of the products of reaction. When the reaction became slow, the oxidised coal was heated in a vacuum to a higher temperature (below the temperature of decomposition of the coal-substance), cooled to the original reaction temperature, and oxygen again admitted. This procedure was repeated several times.

The experiments can be divided into two main groups: (1) with newly-won coal, the vitrain portion of the Hamstead (Brazills) seam, Staffs.; and (2) with vitrain from the same seam after it had been transformed into soluble ulmins by prolonged atmospheric oxidation at 150° (see Francis and Wheeler, *loc. cit.*).

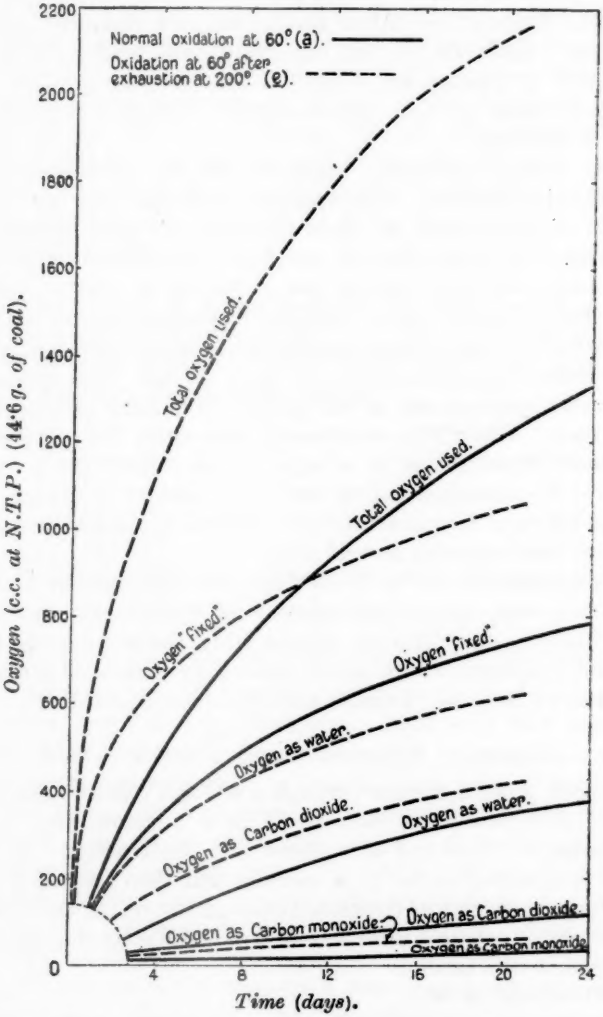
Series I. Experiments with Newly-won Coal.

The coal, ground to pass through a 40- and remain on a 60-mesh sieve (I.M.M. standard), was dried in a vacuum over sulphuric acid during 14 days and introduced into the reaction tube, where it was first heated at 60° in a vacuum and then treated with pure dry nitrogen, which was circulated through the rest of the apparatus. The weight of dry coal used was 44·6 g. The following sequence of experiments was made:

(*a*) Oxidation at 60°.
(*b*) Exhaustion at 100°, followed by oxidation at 60°.
(*c*) Exhaustion at 100°, followed by oxidation at 60°.
(*d*) Exhaustion at 185°, followed by oxidation at 60°.
(*e*) Exhaustion at 200°, followed by oxidation at 60°.
(*f*) Exhaustion at 200°, followed by oxidation at 60°.

The main results are recorded in Tables I and II and in Figs. 1 and 2, all volumes of oxygen and oxygen-equivalents being reduced to *N.T.P.* throughout. The first oxidation (*a*) at 60° can be

FIG. 1.



regarded as the " normal " oxidation of the coal at that temperature. Its general course is shown in curve *a*, Fig. 1.

Carbon dioxide and monoxide were produced from the first at a rate comparable with that of the disappearance of oxygen, but

TABLE I.

Series I. The Oxidation of Newly-won Coal (44·6 g.) at 60°.

Experiment No.	Duration, days.	Oxygen used, c.c.	Oxygen-equivalent of products, c.c. As H_2O.	As CO_2.	As CO.	Oxygen "fixed," c.c.
(*a*) Normal oxidation ...	35	1544	450	169	40	885
(*b*) After exhaustion at 100° (1st)	28	697	122	91	21	463
(*c*) After exhaustion at 100° (2nd)	26	564	105	72	12	375
(*d*) After exhaustion at 185°	17	781	237	127	21	396
(*e*) After exhaustion at 200° (1st)	21	2173	621	423	67	1062
(*f*) After exhaustion at 200° (2nd)	24	1914	461	403	82	968

TABLE II.

Series I. Products of Decomposition of Oxidised Coal.

Experiment.	Oxygen-equivalent of products, c.c. As H_2O.	As CO_2.	As CO.	Total.
At 100° after oxidation *a*	79·8	39·7	3·5	123
At 100° after oxidation *b*	87·0	45·8	4·2	137
At 185° after oxidation *c*	352·0	269·0	39·0	660
At 200° after oxidation *d*	501·0	595·0	81·0	1177
At 200° after oxidation *e*	332·0	634·0	91·0	1057

the appearance of water in the absorption tubes was more gradual. This was no doubt because the coal, being initially dry, retained some of the water vapour first formed. There is no reason to doubt but that the production of water vapour actually corresponded with the production of oxides of carbon during the early stages as it did throughout the rest of the oxidation. As the reaction proceeded, a smaller proportion of the oxygen used became "fixed."

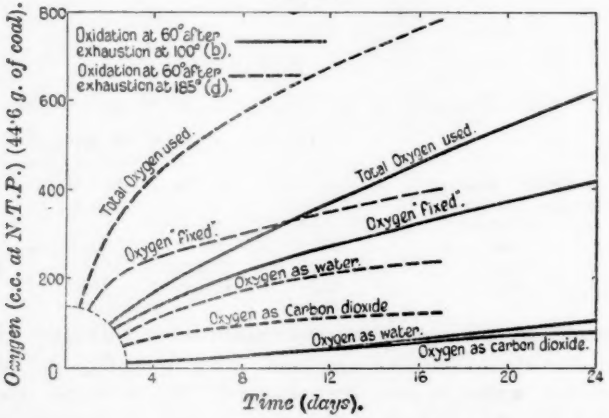
Oxidation was still continuing at a slowly decreasing rate at the end of 35 days, but the experiment was stopped and the apparatus evacuated, the temperature of the coal being raised to 100°. Considerable decomposition of the oxygenated groupings in the coal, equivalent to 123 c.c. of oxygen, occurred (see Table II), 65% of the oxygen thus removed appearing as water, 32·2% as carbon dioxide, and 2·8% as carbon monoxide.

After this exhaustion at 100°, the rate of oxidation at 60° (*b*, Fig. 2) had increased, the "normal" oxidation of the coal being continued, and the oxygen removed from the ulmins by the exhaustion, amounting to about one-seventh of the oxygen fixed during experiment *a*, being simultaneously replaced. Experiment *b* was continued during 28 days, and the coal then again exhausted at

100°. Water and the oxides of carbon were evolved in the same proportions as during the first evacuation, showing that the groupings attacked were of the same character; but rather larger quantities, equivalent to 137 c.c. of oxygen, were obtained owing to the continuance of the " normal " oxidation of the coal.

After this second exhaustion at 100°, the rate of oxidation at 60° (*c*) had again increased, in proportion with the amount of oxygen removed during exhaustion. Estimating, from the oxidation curve for experiment *a*, that during the normal oxidation of the coal the daily fixation of oxygen averaged 12 and 9 c.c. in experiments *b* and *c*, we calculate the fixations consequent on the decompositions at 100° to be 127 and 141 c.c., corresponding with

FIG. 2.



123 and 137 c.c. of oxygen removed during the subsequent decompositions. The oxidation was continued during 26 days and the coal then exhausted at 185°. At this temperature the amount of the " fixed " oxygen released as water and oxides of carbon was considerably greater than at 100°. During experiments *a*, *b*, and *c*, a total of 1723 c.c. of oxygen had become fixed, whilst during the two exhaustions at 100°, 260 c.c. had been released. Of the balance, nearly one-half (660 c.c.) was removed during exhaustion at 185° (see Table II). The proportion of oxides of carbon in the products was greater than at 100°, showing that the character of the groupings decomposed was different.

The rate of oxidation at 60° (*d*) after this treatment was initially very rapid (curve *d*, Fig. 2). This experiment was stopped after 17 days, and the coal then exhausted at 200°. The total amount of oxygen fixed as the result of all the operations up to this point was 1199 c.c. The evacuation at 200° removed as water and

oxides of carbon 1177 c.c., or 98·2%. The proportion of oxides of carbon was greater than at 185°.

Oxidation at 60° (*e*, Fig. 1) was now very rapid. Considerable volumes of oxides of carbon and water were produced from the first, their quantity, in proportion to the amount of oxygen fixed, being greater than in the earlier experiments of the series. After 21 days, 1062 c.c. of oxygen had been fixed, the total amount in the coal being therefore 1084 c.c. (1199 − 1177 + 1062 c.c.). Exhaustion at 200° removed 1057 c.c., or 97·5%. The gases contained a higher proportion of oxides of carbon than those from the previous exhaustion at 200°. Oxidation at 60° (*f*), following this second exhaustion at 200°, was again very rapid. The production of oxides of carbon was greater and that of water was less than in experiment *e*, indicating the gradual elimination of groupings rich in hydrogen.

Series II. Experiments with Coal oxidised at 150°.

The material, 97% of which was soluble in aqueous potassium hydroxide, contained C, 63·8; H, 2·7%. From our previous work, we knew that extensive decomposition of the oxygenated groupings (chiefly carboxylic) of this soluble coal-ulmin would take place on heating in a vacuum. Only 9·76 g. were therefore used for the experiments. The results of a series of oxidations at 60° are recorded in Table III, and those of a series of decompositions at different temperatures in Table IV. No decomposition took place at 100°.

Although during the first oxidation at 60° (*a*), before any heat treatment, some "fixation" of oxygen occurred, there were no gaseous products, and it seems clear that the disappearance of oxygen, half of which occurred whilst it was being admitted into the apparatus, was due to adsorption and solution in the interior of the coal. Exhaustion at 220° caused a partial decomposition of the oxygenated groupings of the ulmin molecule, but the oxygen thus removed, unlike that removed during the corresponding experiments with coal, was not replaced during the subsequent oxidation at 60° (*b*). Physical adsorption of oxygen occurred, whilst there was chemical reaction resulting in the fixation of 4 c.c. of oxygen and yielding traces of oxides of carbon. Possibly water was formed also and retained by the ulmin. Heating at 320° caused considerable decomposition, and, although during the subsequent oxidation at 60° there was appreciable chemical combination with the coal-ulmin, this was by no means as great, having regard to the amount of oxygen previously removed, as might be expected from the results of the experiments with newly-won coal. The

two subsequent exhaustions at 320° (after oxidations *c* and *d*) both caused some decomposition, the volumes of the products being about one-tenth of those yielded during the first exhaustion (after oxidation *b*). These results, and those of the decomposition at 420° and the subsequent oxidation at 60°, emphasise the difference in character between newly-won coal and the soluble coal-ulmin produced from it by oxidation.

TABLE III.

Series II. The Oxidation of Soluble Coal-ulmin (9·76 *g.*) *at* 60°.

Experiment No.	Duration, days.	Oxygen used, c.c.	Oxygen-equivalent of products, c.c. As H_2O.	As CO_2.	As CO.	Oxygen "fixed," c.c.
(*a*) Normal oxidation ...	5	18·4	Nil	Nil	Nil	18·4
(*b*) After exhaustion at 200°	8	22·9	Nil	0·5	Trace	22·4
(*c*) After exhaustion at 320° (1st)	4	53·4	4·4	8·6	8·0	32·4
(*d*) After exhaustion at 320° (2nd)	7	45·4	1·3	4·6	6·0	33·5
(*e*) After exhaustion at 320° (3rd)	5	37·8	Nil	2·1	2·8	32·9
(*f*) After exhaustion at 420°	9	104·4	10·0	12·7	6·4	75·3

TABLE IV.

Products of Decomposition of Soluble Coal-ulmin.

Experiment.	Oxygen-equivalent of products, c.c. As H_2O.	As CO_2.	As CO.	Total.
At 220° after oxidation *a*	60·5	112·5	6·3	179·3
At 320° after oxidation *b*	71·0	381·0	31·0	483·0
At 320° after oxidation *c*	10·6	43·3	5·1	59·0
At 320° after oxidation *d*	14·9	25·0	3·7	43·6
At 420° after oxidation *e*	187·0	420·0	67·5	674·5

We explain the results of the two series of experiments as follows. The oxidation of coal takes place through the medium of an adsorbed layer (compare Tideswell and Wheeler, *loc. cit.*), which almost immediately reacts with certain external groupings of the ulmin molecule, yielding water, carbon dioxide, and carbon monoxide, and forming unstable oxygenated groupings at the points of attack. As the adsorbed layer enters into chemical combination with the coal, it is replaced by a fresh layer, the process being continuous so long as there are groupings remaining with which oxygen can combine at the temperature of experiment. The unstable oxygenated groupings formed are ultimately carboxylic in character and cause the coal-ulmin to become soluble in alkalis.

When the temperature of the coal is raised under vacuum, the oxygenated groupings that have been formed are decomposed, yielding water and the oxides of carbon, the oxygen contained in these being equal in quantity to that " fixed " during the oxidation. The coal now has an increased capacity for retaining oxygen, beyond that due to the normal oxidation, commensurate with the amount removed during exhaustion.

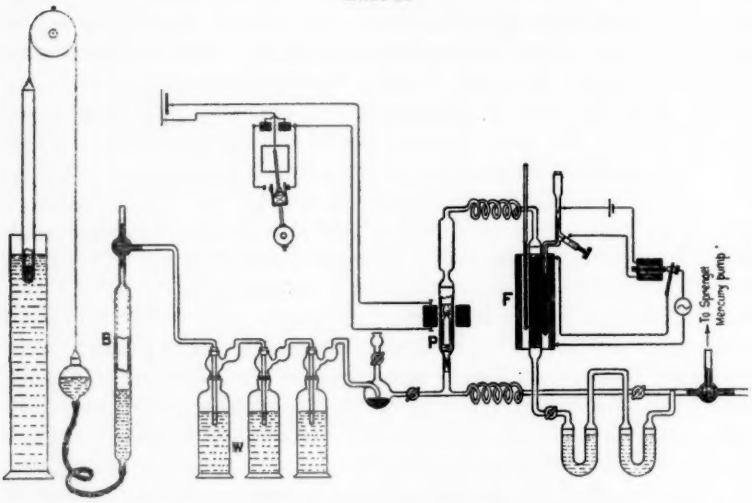
This process of revivification can be repeated many times, but the character of the products of decomposition at each successive exhaustion gradually changes, because groupings of slightly different character are attacked or decomposed. During exhaustion, suitable groupings near those to which oxygen has become attached furnish the hydrogen and carbon required to yield the water and oxides of carbon evolved. During the earlier exhaustions, water is the chief product of decomposition, the action being akin to dehydration. This may result in the formation of internal anhydrides from neighbouring carboxyl groupings, of lactones from suitably placed carboxyl and hydroxyl groups, or of unsaturated groupings such as are produced on the dehydration of β-hydroxy-acids. The number and type of the groupings that can be attacked depend upon the temperature at which oxidation is effected. Oxidation at 60°, as in the series of experiments with newly-won coal, is limited; but at 150°, the temperature employed to produce from that coal the soluble ulmins used for the second series of experiments, all the external groupings of the molecule are eventually attacked, leaving oxygenated (chiefly carboxylic) groupings in their place. No suitable groupings are available in such a fully-oxidised coal for the type of decomposition, permitting almost complete revivification, that obtains with a partly oxidised coal, but the decomposition (at the high temperature required) modifies the ulmin molecule profoundly, leaving a comparatively stable residue, there being but few groupings containing oxygen and hydrogen. Such revivification of this residue as can be effected is of the same character as is obtainable with carbon, and it is probable that the molecular structure of the residue approximates to that of carbon. With coals saturated with oxygen at temperatures between 60° and 150°, different degrees of revivification, by exhaustion at a higher temperature than that of oxidation, are possible.

Experimental.

The circulation apparatus employed for submitting the coal to the action of oxygen differed in many respects from that used by Tideswell and Wheeler (*loc. cit.*). The reaction tube in which the powdered coal was packed was supported vertically within an

electrically-heated furnace (F, Fig. 3), the temperature of which could be maintained constant by means of an electric thermostat. The lower end of the reaction tube was connected by ground-glass joints to two weighed U-tubes in series. The first contained granular calcium chloride for the absorption of water, and the second, asbestos impregnated with sodium hydroxide (the top of each limb being covered by a layer of granular calcium chloride) for the absorption of carbon dioxide. These U-tubes were duplicated so that they could be periodically removed for weighing and fresh ones substituted.

FIG. 3.



Circulation of the oxygen through the coal and absorption tubes was effected by an electrically-operated glass pump, P, of special construction (see Francis, *Fuel*, 1926, **5**, 39). The oxygen entering the apparatus was first dried by bubbling through shallow layers of concentrated sulphuric acid contained in a series of large wash-bottles, W, and then passed through a mercury seal of about 1 mm. The charges of oxygen required for an experiment were contained in a graduated burette, B, over a mixture of equal parts by volume of glycerol and water. The reservoir of this burette was supported by a cord which passed over a pulley to a counterweight consisting of a tube, containing mercury, which dipped into a deep jar containing glycerol and water. The external diameter of the counterweight was equal to the internal diameter of the burette, so that as the level of the liquid in the burette rose, consequent on absorption of oxygen by the coal, the reservoir rose an equal amount and the pressure was maintained constant. The pressure was adjusted at

the beginning of an experiment to be just sufficient to force the oxygen through the layers of sulphuric acid and the mercury seal.

As absorption by the coal proceeded, oxygen was drawn into the apparatus to maintain a constant pressure. The volume thus entering was measured periodically on the burette. Corrections were made for variations in atmospheric temperature and pressure and for the vapour pressure of the liquid in the burette. The oxygen, which was prepared by the action of a solution of potassium permanganate on a mixture of hydrogen peroxide and dilute sulphuric acid, was of 99·5% purity. Simultaneously with the measurements of the oxygen used, the weights of water and carbon dioxide formed were determined from the increase in weight of the U-tubes, and a sample of the circulating gases was analysed to determine the amount of carbon monoxide formed.

At the conclusion of an oxidation experiment, the apparatus was rapidly evacuated and the coal then raised to the required temperature during 30 hours, the gases evolved being drawn, by means of a Sprengel mercury pump, through the weighed U-tubes. Water and carbon dioxide were thus absorbed and estimated, and carbon monoxide was collected and measured.

The work described in this paper forms part of a research on the spontaneous combustion of coal which we are carrying out for the Safety in Mines Research Board, to whom our thanks are due for permission to publish it.

SAFETY IN MINES RESEARCH LABORATORIES,
SHEFFIELD. [*Received, September 19th*, 1927.]

CCCXCIV.—*The Ternary Systems Copper Acetate–Acetic Acid–Water and Lead Acetate–Acetic Acid–Water at* 25°.

By KARL SANDVED.

IN connexion with a study of the relation between lead chloride and lead acetate in aqueous solution, the system lead acetate–acetic acid–water was examined, and also, for the sake of completeness, the system copper acetate–acetic acid–water. The results form the subject of the present communication.

The acetate–acetic acid–water systems investigated previously are of the same general type (Sodium salt: Dukelski, *Z. anorg. Chem.*, 1909, **62**, 114; Dunningham, J., 1912, **101**, 431. Ammonium salt: Ruth Sugden, J., 1926, 960. Silver salt: Knox and Will, J., 1919, **115**, 853), all obeying the following two rules: (1) The

solubility of the acetate is depressed on addition of acetic acid, as would be expected from the classical solubility laws; (2) acid acetates occur in the solid phase at a certain concentration of acetic acid.

Of the systems described in the present communication, the copper acetate system conforms completely to these rules, whereas the lead acetate system shows a totally different behaviour. The exceptional complexity of lead acetate solutions has frequently been described. A complete investigation of the ternary system lead acetate–acetic acid–water throws some light upon the constitution of these solutions, and provides data bearing on the existence or non-existence of acid lead acetates, which have not hitherto been described.

Experimental.

Copper Acetate–Acetic Acid–Water at 25°.

The following neutral and acid salts have been described: $Cu(C_2H_3O_2)_2$ (Tilden, J., 1884, **45**, 266), $Cu(C_2H_3O_2)_2,H_2O$ (Gerhardt, *J. Pharm.*, 1845, **9**, 50), $Cu(C_2H_3O_2)_2,5H_2O$ (Wöhler, *Pogg. Ann.*, 1836, **37**, 166; Astre, *J. Pharm. Chim.*, 1893, **28**, 542), $Cu(C_2H_3O_2)_2,2HC_2H_3O_2,H_2O$ (Villiers, *Compt. rend.*, 1877, **85**, 1236).

The mixtures were shaken in a thermostat at 25° ± 0·05°. The equilibria were completely established in 5 to 6 hours, except in solutions containing more than 90% of acetate, which required about 24 hours. The solid was allowed to settle, and the clear solution was drawn off and analysed. The solid was then rapidly drained on a Buchner funnel and analysed, the composition of the dry solid being found by Schreinemakers's method (*Z. physikal. Chem.*, 1893, **11**, 81). Copper was estimated by electrolytic deposition from dilute sulphuric acid solution (see Fischer, *Z. angew. Chem.*, 1907, **20**, 134), whilst the total acetic acid was estimated by distillation with phosphoric acid, as described by Dukelski (*loc. cit.*).

The copper acetate used was the purest obtainable from British Drug Houses, Ltd. Estimations of copper and acetic acid were in accord with the formula $Cu(C_2H_3O_2)_2,H_2O$. The anhydrous acetate was prepared by heating the monohydrate for 5 hours at 95—100° (Angel and Harcourt, J., 1902, **81**, 1385; Tilden, *loc. cit.*). Analysis then gave Cu, 34·9, 34·8, 34·9, 34·91, 34·9 (mean, 34·9) [Calc.: Cu, 35·0%]. This anhydrous copper acetate was employed for solutions corresponding to the extreme right side of the diagram.

The experimental results are in Table I, and Fig. 1 shows the corresponding graph, constructed according to Lodočnikow's method (*Z. anorg. Chem.*, 1926, **151**, 181). If, in order to show more clearly the varying composition of the saturated solutions, the scale is

increased ten times (see right-hand ordinates), the broken line in Fig. 1 is obtained. It is seen that three compounds are capable of existence, *viz.*, (1) $Cu(C_2H_3O_2)_2,H_2O$ (marked 1 in the figure); (2) $Cu(C_2H_3O_2)_2,HC_2H_3O_2,H_2O$ (marked 2); (3) $Cu(C_2H_3O_2)_2,HC_2H_3O_2$ (marked 3).

FIG. 1.

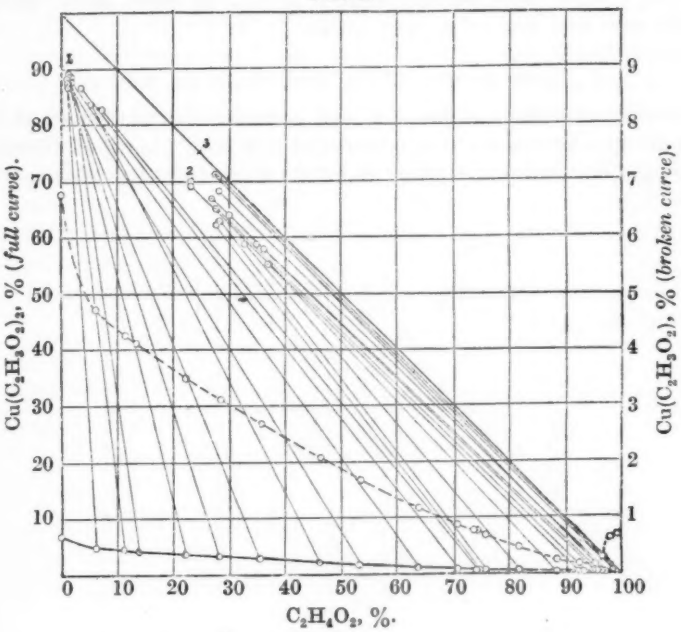


TABLE I.

The Ternary System $Cu(C_2H_3O_2)_2$–$HC_2H_3O_2$–H_2O at 25°.

Liquid.		Wet solid.		Liquid.		Wet solid.	
%$CuAc_2$.	%HAc.	%$CuAc_2$.	%HAc.	%$CuAc_2$.	%HAc.	%$CuAc_2$.	%HAc.
6·79	—	76·02	0·09	0·69	75·74	62·95	28·12
4·73	6·18	88·32	0·82	0·48	81·60	58·87	32·57
4·27	11·14	86·70	1·03	0·25	88·46	65·11	27·96
4·16	13·65	89·31	1·04	0·22	92·17	55·45	36·97
3·49	22·35	87·85	1·64	0·21	93·33	63·87	29·96
3·12	28·43	88·62	1·57	0·20	94·94	59·04	34·81
2·68	35·53	87·53	0·94	0·21	95·26	66·68	26·67
2·10	46·08	83·70	5·10	0·17	95·40	35·94	58·09
1·70	53·35	88·00	1·81	0·23	95·66	69·01	23·30
1·18	63·67	88·31	0·93	0·23	96·37	71·50	27·49
0·89	70·81	86·60	3·45	0·31	97·20	68·25	28·10
0·79	74·06	82·90	7·20	0·71	98·77	70·91	28·31
0·77	74·42	62·10	27·59	0·71	98·91	70·58	28·01

The ternary invariant point between (1) and (2) lies at 0·79% $Cu(C_2H_3O_2)_2$ and 74·06% $HC_2H_3O_2$, and that between (2) and (3) at

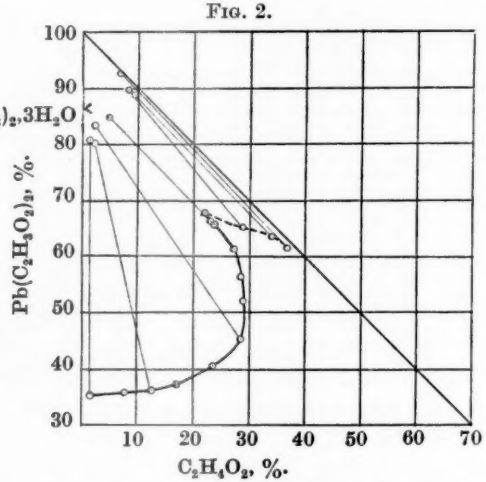
0·17% $Cu(C_2H_3O_2)_2$ and 95·40% $HC_2H_3O_2$. The solubility of copper acetate in water at 25° is 6·79%.

The pentahydrate described by Wöhler and by Astre (*locc. cit.*) is not stable as a solid at 25°. Fig. 1 shows, moreover, that the acid salts obtained are not of the same type as that described by Villiers (*loc. cit.*), for no acid salt is indicated containing more than 1 mol. of acetic acid to 1 mol. of copper acetate.

Lead Acetate–Acetic Acid–Water at 25°.

Numerous basic and neutral lead acetates are mentioned in the literature, whereas no acid compound has been identified (Gmelin-Kraut, "Handbuch," 1924). Sakabe (*Mem. Coll. Sci. Kyoto*, 1914,

FIG. 2.



1, 57) has investigated the system lead oxide–acetic acid–water, but his data do not go beyond 19·28% of free acid. Moreover, his figures do not agree either with the results of the present work or with those obtained by Jackson (*J. Amer. Chem. Soc.*, 1914, **36**, 2346) for the system lead acetate–lead oxide–water. Thus Sakabe found the solubility of lead acetate to be about 6·5%, whereas the true solubility is about six times as high. Further, Sakabe employed ignited lead oxide for his experiments and probably true equilibria were not attained owing to the inactivity of the oxide.

The lead was estimated as sulphate according to the recognised method. For the estimation of acetic acid, an excess of *N*/5-sulphuric acid was added to the solution, which was then diluted with twice its volume of alcohol and titrated with *N*/5-sodium hydroxide (free from carbon dioxide) and phenolphthalein. (The addition of alcohol produced a very sharp end-point.) Boiled

water only was used, and all flasks were fitted with tight glass stoppers. In order to check the method, titrations were carried out with pure lead acetate from the British Drug Houses: the alkali required for back titration was always equivalent to the amount of acid added. Anhydrous lead acetate was prepared by heating the trihydrate at 130°. Three estimations of lead in the dried product gave 63·7, 63·7, 63·7 [Calc.: Pb, 63·7%].

As may be seen from Table II and Fig. 2, the solubility of lead acetate increases on addition of acetic acid, at first rather slowly, but from 20% acetic acid very sharply. The maximum percentage of acetic acid is at 28·99%, which consequently is the highest possible content of acetic acid in presence of lead acetate trihydrate as a solid at 25°, owing to the high solubility of the latter. By dissolving the trihydrate in glacial acetic acid, a point was finally reached corresponding to 67·90% $Pb(C_2H_3O_2)_2$ and 22·01% $HC_2H_3O_2$, marked * in Table II. Anhydrous lead acetate was used

TABLE II.

Liquid.		Wet solid.		Liquid.		Wet solid.	
$\%PbAc_2$.	%HAc.	$\%PbAc_2$.	%HAc.	$\%PbAc_2$.	%HAc.	$\%PbAc_2$.	%HAc.
35·50	1·61	80·80	1·35	61·48	27·10		
35·62	7·82			65·84	23·62	84·63	4·87
36·08	12·56	80·05	2·39	66·48	22·98		
37·10	17·04			*67·90	22·01		
40·58	23·58			65·09	28·90	89·85	8·05
45·39	28·55	83·39	2·73	63·55	34·00	88·70	9·28
52·10	28·99			61·50	36·77	92·61	6·81
56·50	28·41						

for the extreme part of the diagram; it dissolved very slowly in concentrated acid, 2 days being necessary for the attainment of constant values. The solution always showed a slight turbidity, which rendered separation of the two phases impossible at the highest concentrations of acid. This part of the curve, being less trustworthy, has been drawn as a broken line in Fig. 2, but it nevertheless shows that anhydrous lead acetate is still present as a solid and that no acid compounds can be prepared in this way. In order to check this result, the anhydrous salt and glacial acetic acid were boiled together for 5 hours, but the high viscosity and density of the solution prevented the separation of the solid from the liquid. The appearance of the solution was not perceptibly altered after 3 weeks, and it was quite impossible to effect any crystallisation in this highly supersaturated solution. It may be emphasised that these experiments do not definitely prove the non-existence of acid lead acetates. The velocity of reaction in such viscous systems is so depressed that true equilibria may not be reached.

Discussion.

The abnormal behaviour of lead acetate solutions has been long known. Measurements of electrolytic conductivity (Noyes and Whitcomb, *J. Amer. Chem. Soc.*, 1905, **27**, 747) and of *E.M.F.* (Conrad, Diss., Göttingen, 1903) indicate a low concentration of free lead ions in these solutions : according to Noyes and Whitcomb the degree of dissociation in *N*-solution is about 17%.

These results are in agreement with the changes which occur when lead salts and acetates are brought together. The increased solubility of lead sulphate in ammonium acetate (Carius, *Annalen*, 1863, **125**, 87) is explained by Noyes and Whitcomb as due to the formation of un-ionised lead acetate by metathesis; and a similar assumption was made by Fox (J., 1909, **95**, 878) to account for the solubility of lead sulphate in alkali acetate solutions.

Several other authors have maintained, however, that various other factors, besides the low degree of dissociation, have to be considered in such solutions. White (*Amer. Chem. J.*, 1904, **31**, 4; 1906, **35**, 218) explains the increased solubility of lead chloride in lead acetate solutions, as well as the type of double compound isolated, by assuming complex ions to be present in the solution. (The author hopes to publish the results of a phase-rule study of this system.)

Further evidence on the existence of complex ions has been given by Blomberg (*Chem. Weekblad*, 1914, **11**, 1030; *Z. Elektrochem.*, 1915, **21**, 438), Conrad (*loc. cit.*), and Labendzinski (Diss., Breslau, 1904). By postulating the equilibria

$$(1)\ 2Pb(C_2H_3O_2)_2 \rightleftharpoons Pb(C_2H_3O_2)^{\cdot} + Pb(C_2H_3O_2)_3'$$
$$(2)\ Pb(C_2H_3O_2)^{\cdot} \rightleftharpoons Pb^{\cdot\cdot} + C_2H_3O_2'$$
$$(3)\ Pb(C_2H_3O_2)_3' \rightleftharpoons Pb(C_2H_3O_2)^{\cdot} + 2C_2H_3O_2'$$

Blomberg is able to account for the abnormal solubility data as well as for the electrochemical measurements referred to previously.

As shown by Hill (*J. Amer. Chem. Soc.*, 1917, **39**, 218), the conditions are altogether different when acetic acid is used instead of alkali acetates; thus, the solubility of lead chloride increases slightly on addition of small amounts of acetic acid, and then falls regularly on further additions (see Herz and Martin, *Z. anorg. Chem.*, 1924, **140**, 339). Hill points out that the theory of metathesis predicts an increase of solubility and therefore can hardly be valid; he suggests, furthermore, that the grounds for these anomalies lie in deviations from the mass-action law. Experiments carried out in connexion with the present work show that the solubility of lead sulphate is depressed in a similar way on addition of acetic acid.

It seems evident, however, that these facts do not by any means

disprove Noyes and Whitcomb's hypothesis. All the data available on lead acetate solutions show that this salt, even when regarded as a ternary electrolyte, is more extensively dissociated than acetic acid. Hence the equilibrium $PbCl_2 + 2HC_2H_3O_2 \rightleftharpoons Pb(C_2H_3O_2)_2 + 2HCl$ will give very small amounts of lead acetate in the solution. The slight formation of lead acetate is, however, probably the cause of the increased solubility on the first part of Hill's curve.

When strong electrolytes such as alkali acetates are used instead of acetic acid, the conditions are evidently completely altered, and in this case the acetate ions will have to unite with the lead ions to a considerable extent. In the author's opinion, the increased solubility of sparingly soluble lead salts in solutions of alkali acetates is chiefly due to this combination of ions. It does not appear reasonable that this reaction leads to the formation of undissociated lead acetate only, as originally supposed by Noyes and Whitcomb, but rather to univalent ions $Pb(C_2H_3O_2)^{\cdot}$. By considering lead acetate as a binary electrolyte, it is possible to interpret more satisfactorily the results obtained from conductivity measurements. The degree of dissociation calculated on this assumption is about 70% in *N*-solutions, giving the maximum upper limit of this primary dissociation. The measurements by Conrad (*loc. cit.*) seem to show that the second dissociation takes place only to a slight extent.

Fox (*loc. cit.*) gives the following solubilities of lead acetate in potassium acetate solutions at 25° :

$KC_2H_3O_2$, %	0	13·87	15·40	
$Pb(C_2H_3O_2)_2$, %	35·90	38·05	36·91	

Data for the solubility in sodium acetate solutions at 25° have now been obtained :

$NaC_2H_3O_2$, %	0	4·81	15·37	15·96
$Pb(C_2H_3O_2)_2$, %	35·75	35·23	43·28	38·85

If these figures are compared with those in Table II, it will be seen that alkali acetates and acetic acid have approximately the same effect upon the solubility of lead acetate. In the former case, however, the maximum solubility will be reached at a comparatively low concentration of alkali acetate due to changes in the solid phase It will be seen also that the first addition of sodium acetate causes the solubility to fall slightly, while an increase occurs on further addition. This fact seems to be satisfactorily accounted for by the theory of Blomberg (*loc. cit.*). The first quantity of sodium acetate will depress the dissociation of the $Pb(C_2H_3O_2)^{\cdot}$ ion (2), whereas at higher concentrations of acetate ions, and consequently of $Pb(C_2H_3O_2)^{\cdot}$ ions, the formation of complex ions, $Pb(C_2H_3O_2)_3'$, and undissociated molecules (1 and 3) will be predominant. In the case

of acetic acid, the first effect due to the increase in acetate ions will naturally disappear, causing the solubility to increase continuously throughout the whole range.

The extraordinary solubility of lead acetate in acetic acid can hardly be accounted for in any other way than by assuming the occurrence of molecular changes. Differences in the thermodynamical and electrical properties of water and acetic acid (Webb, *J. Amer. Chem. Soc.*, 1926, **48**, 2263) scarcely suffice to explain deviations of the observed magnitude, nor does it seem that the basic character of lead acetate solutions can be of essential importance (Löfman, *Z. anorg. Chem.*, 1919, **107**, 241). Webb (*loc. cit.*) has pointed out that strong electrolytes, such as lithium iodide or nitrate, most probably are incompletely dissociated in glacial acetic acid. It seems therefore plausible to assume that complex salts of the type $x\mathrm{HC_2H_3O_2},y\mathrm{Pb(C_2H_3O_2)_2}$ would be almost undissociated in concentrated acetic acid solution. The failure to isolate any acid salts from these solutions points to a very high solubility of the complex compounds, as may be expected from the modern theories on solubility. A symmetrical combination of the type AcPbAc, in which the lead atom is entirely surrounded by acetate groups, will show in respect to its electrical and thermodynamical properties a close similarity to pure acetate groups, and hence have a special ability for penetrating a field built up by such groups.

Summary.

The two ternary systems copper acetate–acetic acid–water and lead acetate–acetic acid–water have been investigated at 25°. The first system belongs to the same type as the alkali acetate–acetic acid–water systems, whereas the second shows totally different properties, in accordance with the generally abnormal character of lead acetate solutions.

It is suggested that this abnormal behaviour is best accounted for by the assumption of molecular changes, and it is pointed out that the supposed non-validity of the mass-action law is insufficient to explain deviations of the observed magnitude.

The author's thanks are due to the Ramsay Memorial Fellowship Trust for placing a fellowship at his disposal, and to Professor J. C. Philip, F.R.S., under whose interested and valuable direction this research was conducted.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, October 21st*, 1927.]

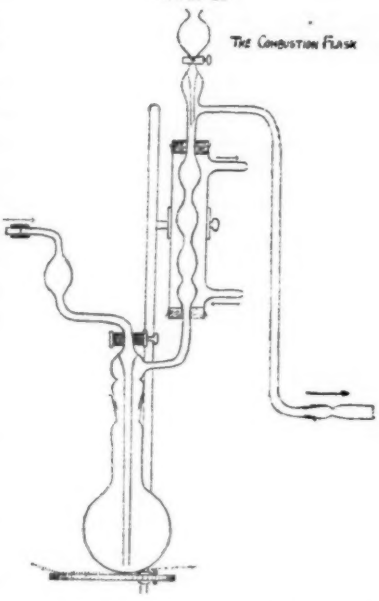
CCCXCV.—*The Determination of Total Carbon and Carbon Dioxide in Small Quantities of Soil Solutions.*

By Colin Falconer Flint.

During the course of a research on the ultimate composition of the soil solution, a method was needed for the determination of total carbon, which was present to the extent of 100—1000 parts per million parts whilst the quantity available for a determination was usually less than 10 c.c. The ordinary permanganate oxidation method used in water analysis did not yield concordant results.

The wet combustion method used in steel analysis (see Corleis, *Stahl u. Eisen*, 1894, **14**, 581; Treadwell–Hall, "Analytical Chemistry," vol. 2, 5th ed., p. 399, New York, 1919) was adapted to the routine examination of soil solutions containing nitrate and chloride as high as 3000 parts of NO_3 and 800 parts of Cl per million. This was achieved by using in the combustion-furnace tube a 6-inch cylinder of reduced copper gauze together with either copper oxide and a spiral of silver gauze or an 8-inch cartridge of lead chromate (see Thorpe and Whiteley, "Manual of Organic Chemical Analysis," London, 1926). The method was then used in the routine examination of a large number of soil solutions for total carbon, and a part of the apparatus was further adapted to the determination of carbon dioxide.

Fig. 1.



Experimental.

(1) *Total Carbon.*—The train of apparatus employed was as follows, in the order indicated: A soda–lime tower, a set of 3 potash bubblers, the combustion flask (Fig. 1) attached through a ground joint to the hard glass combustion tube heated in a light Dennstedt furnace, a sulphuric acid bubbler, a glass-stoppered U-tube containing pumice soaked in sulphuric acid, and glass-stoppered absorption and trap tubes, charged with "Sofnolite" or soda–lime and

topped with calcium chloride. Proper attention was directed to sieving the charges for these tubes and to regulating the speed of the air current; otherwise, fine dust was swept out, causing serious losses. A current of 4 bubbles a second in the bubbler was the fastest consistent with safety, and was used throughout, being regulated by a screw clip before the pumice tube.

50 C.c. of water, 15 c.c. of saturated pure chromic acid solution, and 120 c.c. of pure sulphuric acid were boiled gently in the combustion flask for 10 minutes with the tap-funnel open. The chromate cartridge was then heated to dull redness while a current of purified air was drawn through the apparatus for 20 minutes, the flask being allowed to cool. Next, the tap on the pumice tube was closed, the freshly reduced copper spiral was inserted and heated over a faintly luminous flame that just touched the trough, and the absorption and guard tubes were placed in position. The soil solution was placed in the tap-funnel and drawn into the system, admission of air being avoided, and the funnel was rinsed with a few drops of water. The air current was started again, and the flask boiled over a small flame for 1½ hours. The pumice tube was then closed, the tap-funnel opened, and the absorption tube removed and weighed.

If the initial boiling-out had not been carefully performed, the evolution of gas from the combustion mixture was frequently so rapid as to blow the mixture back into the potash bulbs; this could be controlled to some extent by removing the burner and fanning the flask.

The following figures for blank determination and determinations of total carbon in a standard sugar solution and a soil extract are typical of the results obtained.

The method was tested on sucrose in an apparatus having rubber connexions to the furnace, instead of ground glass joints, and both with and without a reflux condenser. 10 C.c. of sugar solution, containing carbon equivalent to 27·7 mg. of carbon dioxide, and 5 mg. each of NO_3 and Cl, gave 27·2 mg. of carbon dioxide (without reflux) and 28·0 mg. (with reflux); 20 c.c. of liquid gave 55·6 mg. of carbon dioxide. This apparatus, as well as that shown in Fig. 1, gave less than 0·1 mg. increase in weight in blank determinations with the reagents when as much as 0·1 g. of potassium nitrate and 0·05 g. of potassium chloride were used. With the apparatus figured, 5 c.c. of a certain soil solution gave 1·6 mg. of carbon dioxide consistently.

Good agreement was obtained in repeated tests. The errors did not exceed 0·3 mg. with the largest quantities of carbon, which in general yielded 1—30 mg. of carbon dioxide.

(2) *Carbon Dioxide.*—The apparatus was adapted to the deter-

mination of carbon dioxide by cutting the horizontal delivery tube about 1 inch from the reflux condenser and connecting it to the drying and absorption train by means of a rubber joint. To prevent bumping in the solution on boiling, hydrogen was liberated by the action on aluminium of the hydrochloric acid with which the solution was acidified; this metal was chosen for its freedom from surface contamination of carbonate or sulphide. Very dilute acid was used in order to avoid a too rapid evolution of gas. The complete expulsion of carbon dioxide from the system was accelerated by the current of air and the generation of hydrogen, but boiling was continued for 1½ hours as an additional precaution.

100 C.c. of water and 5 c.c. of hydrochloric acid were boiled for 20 minutes in the current of air after ½ inch of 16-gauge aluminium wire had been placed in the exit tube from the reflux condenser; without stopping the boiling, the pumice tube was closed to allow the absorption and guard tube to be inserted; the sample of the soil solution was drawn into the system, and the wire was dislodged from its position and caused to fall into the mixture. (This procedure avoided all danger of "blowing back.") The boiling was continued for 1½ hours, then the absorption tube was weighed.

Since blank determinations gave less than 0·1 mg. increase in weight of the absorption vessels, this method was applied to soil solutions, 10 c.c. being used for each test. With soil solutions of $p_H < 7$, the total carbon dioxide so found did not exceed a few parts per million.

During the publication of this work, a method was described (Nicloux, *Bull. Soc. Chim. biol.*, 1927, **9**, 639) for the rapid and accurate determination of a maximum of 3 mg. of carbon present as organic matter in 1 c.c. of aqueous solution. The chromic–sulphuric acid oxidation takes place in a vacuum, and is catalysed by silver chromate. A method for the micro-determination of carbon dioxide was also described (*ibid.*, p. 758).

ROYAL COLLEGE OF SCIENCE,
LONDON, S.W. 7.

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Revised, November 16th, 1927.]

CCCXCVI.—*The Critical Temperatures of Boron Trichloride and Silicon Tetrachloride.*

By THOMAS WALLACE PARKER and PERCY LUCOCK ROBINSON.

AN investigation involving the determination of critical temperatures is in progress in this laboratory, and these results are submitted because no previous determination appears to have been made in

the case of boron trichloride, whilst the only one relating to silicon tetrachloride is that of Mendeléev (*Annalen*, 1861, **119**, 11). Carefully purified material has been used in each case, and the thermometers have been standardised at or very near to the readings actually used by the National Physical Laboratory, so that considerable trust may be placed in these values.

Experimental.

Preparation of Materials and Filling of Tubes.—The Durosil glass-ware used in these operations was cleaned by treatment with chromic–nitric acid mixture, well washed with numerous changes of water, the last portions being good distilled water, and with alcohol and ether, after which it was dried by heating to 110° in an electric oven.

Boron trichloride. About 120 c.c. of boron trichloride, which had been used for an approximate determination of density (see Briscoe, Robinson, and Smith, this vol., p. 284) and had remained sealed under vacuum in a container provided with a special joint, constituted the initial material for this work. This liquid was subjected to two successive fractional distillations in a vacuum, head and tail fractions of about 5 and 10 c.c. respectively being rejected on each occasion, and the main fractions being received into vessels having special joints. The fractionations were performed with the usual precautions taken in this laboratory and described elsewhere for ensuring the absence of leaks in the train, of moisture on the interior surface of the vessels, and of residual air. The vessel, L, containing the main fraction (90 c.c.) was now attached to the train illustrated in Fig. 1; B_1—B_8 represent the various critical-temperature tubes, with walls 1 mm. thick and bore 4—5 mm., and provided with the thickened capillaries necessary for sealing off under a vacuum; M is the surface-tension vessel previously described (Mills and Robinson, this vol., p. 1823); and N is a vessel with a special joint for receiving the surplus material. This train was evacuated and slowly refilled with dry air 6 times while at 150°, to ensure careful drying, and was sealed off from the pump under the highest vacuum attainable. The special joint was then broken, and the liquid was distilled, solid carbon dioxide–ether being used as refrigerant, into tubes B_1, B_2, and B_3; M was then filled to the requisite level and removed; next, B_4, B_5, B_6, and B_7 were filled and removed in the order indicated, and, the major portion of the residual liquid having been distilled into N, which was drawn off, B_8 was filled and removed. The normal procedure in charging the critical-temperature tubes was

to fill them with liquid and then distil back to the main bulk until the desired quantity remained in the tube, the final sealing being done without arrest in the backward flow of vapour. It could thus be reasonably presumed that the tubes contained only the slightest trace of air, if any at all.

Silicon tetrachloride. The material used was the head fraction of silicon tetrachloride obtained from the second vacuum distillation of the U.S.A. sample (see Robinson and Smith, J., 1926, 1272) and was considered of sufficient purity for immediate use. A train

FIG. 1.

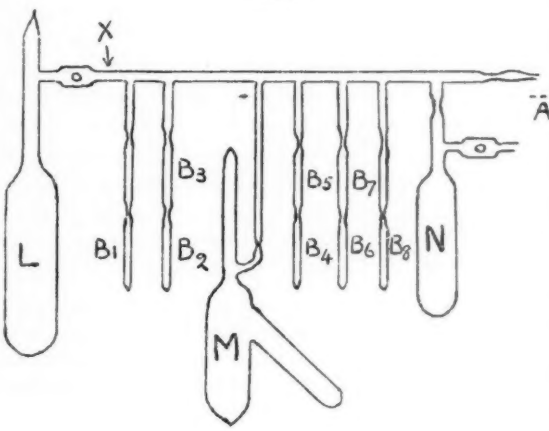
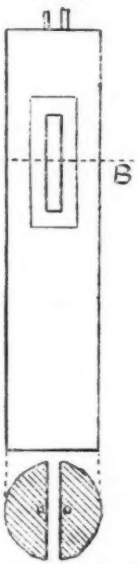


FIG. 2.



Elevation and Section through AB.

similar to Fig. 1 was employed. A head fraction of 2 c.c. was first taken in N, tubes B_1, B_2, B_3, and B_4 were successively filled and removed, and then M was filled. As described elsewhere (Mills and Robinson, *loc. cit.*), when M had received sufficient liquid a fracture occurred in the special joint of L and this vessel was at once drawn off at X, the apparatus was immediately attached to the pump at B_8, rapidly evacuated, and sealed off above this point, after which M was removed. This unfortunate accident rendered it impossible to fill further tubes.

Critical-temperature Apparatus and Phenomena.—Apparatus. This was a modification of that of Hackspill and Mathieu (*Bull. Soc. chim.*,

1919, **25**, 482). A cylinder of copper (Fig. 2), 5 cm. × 27 cm., with a central hole 11 mm. in diameter and two other holes 7 mm. in diameter and reaching almost to the bottom, was constructed for us in the Department of Engineering by the courtesy of Prof. C. J. Hawkes. The metal between the outer and the central holes was 2 mm. at the thinnest parts. A window, 4 cm. high and the width of the central hole, was cut completely through the metal about 10 cm. from the top. This window was closed by thick sheets of colourless mica, bound in position by means of copper wire. The critical-temperature tube was placed in the central hole, and rested on a length of glass rod at a height convenient for observation. The thermometers were similarly supported in the side holes, so that the bulbs were level with the middle of the critical-temperature tube, correction for exposed stem being made when necessary. The apparatus with the tube and thermometers in position was placed inside a heater (kindly lent to the authors by Dr. L. A. Sayce) consisting of a sheet-copper cylinder 22 in. × 6 in., fitted on opposite sides with vertical glass windows 1 in. wide, and heated by a spiral winding of nichrome wire insulated from the copper by a layer of asbestos board. The bottom was well lagged and a lid of several thicknesses of asbestos board closed the top. This arrangement, used with suitable external resistances, was found to change the temperature of the metal cylinder very slowly and uniformly, while tests made by changing the thermometers from hole to hole showed that under the conditions prevailing during the experiments, a difference in temperature of less than $\pm$ 0·1° was to be expected in the three positions.

Phenomena. Young (*Phil. Mag.*, 1906, **20**, 803) and Travers and Usher (*Proc. Roy. Soc.*, 1906, **78**, 247) seem to have found the phenomena attending the change of state susceptible of much sharper observation than did Hackspill and Mathieu (*loc. cit.*), who state that it is difficult to observe the critical phenomena to less than $\pm$ 1·0°. The present authors, in common with most observers, have taken the temperature recorded at the appearance of the meniscus in the cloud during the change from vapour to liquid as the critical temperature. This phenomenon was observed against a bright background, and as there was an easily perceptible change during a fall of 0·2°, it is probable that the individual readings for identical conditions of the cloud were within $\pm$ 0·1° of the actual temperature. This is probably much beyond the constancy to be expected in the temperature at which identical appearances occur in separate experiments. Tubes filled to the extent of one-third of their volume gave the most satisfactory critical phenomena. The results are in the table.

Liquid.	Tube.	Successive observations at same heating.						Mean.
BCl_3	B_2	178·8°	178·7°	178·7°				178·7°
	B_4	178·9	178·9	178·8				178·9
	B_5	178·7	178·7	178·7				178·7
	B_6	178·9	178·8	178·7				178·8
$SiCl_4$	C_2	233·5	233·5					233·5
	C_3	233·6	233·5	233·5				233·5
	C_4	233·9	233·8	233·8	233·6°	233·6°	233·5°	233·7

The results for boron trichloride do not indicate any real difference from tube to tube, and give a mean value 178·8° ± 0·2°, but they do show that there is a tendency for the value to fall if the material is maintained at or about the critical temperature for some time. Two days before the determinations for B_2 given above, the tube was accidentally heated to 210° and then gave two successive results of 178·4°. There is some reason to suppose that the regular differences in the critical temperature observed in successive heatings, although not much greater than the probable experimental error, may in fact be real. If so, it appears that heating the liquid to a higher temperature causes a depression of the critical temperature which may be due to a change in the physical properties of the liquid, but which, in the opinion of the authors, is not caused, in the case of a compound such as boron trichloride, by thermal dissociation. Similar differences are shown in the case of silicon tetrachloride, particularly in tube C_4. The mean value of the critical temperature is 233·6° ± 0·2°, which is rather higher than that due to Mendeléev (*loc. cit.*).

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-UPON-TYNE. [*Received, August 5th*, 1927.]

CCCXCVII.—*The Complex Cyanides of Molybdenum.*

By WILLIAM RALPH BUCKNALL and WILLIAM WARDLAW.

SPECIAL interest is attached to the complex cyanides of molybdenum and tungsten, $R_4Mo(CN)_8$ and $R_4W(CN)_8$, for few cyanides of quadrivalent elements exist, and complex cyanides are known only in isolated cases. Moreover, these complex salts represent well-substantiated examples of a co-ordination number of 8, and the exceptional stability of the complex ions $[Mo(CN)_8]''''$ and $[W(CN)_8]''''$ finds a satisfactory explanation in the modern electronic theory of valency. Undoubtedly this marked stability is intimately associated with the fact that the cyanide units are regularly distributed round a central metallic atom, of which the effective atomic number—in the case of molybdenum, 54, and of tungsten, 86—is that of the next higher inert gas.

The abnormal behaviour of these complex cyanides on oxidation with acid permanganate has been the subject of much theoretical speculation. Unlike the majority of compounds containing molybdenum and tungsten, which on oxidation with acid permanganate are converted into the sexavalent condition, these complex cyanides pass only to the quinquevalent state. In order to dispel any doubt as to the correctness of formulating the complex tungsten cyanide, $K_4W(CN)_8$, as a derivative of quadrivalent tungsten, Olsson (*Ber.*, 1914, **47**, 917; *Z. anorg. Chem.*, 1914, **88**, 49) showed that on complete oxidation with ammoniacal silver salt solution, two atoms of silver separated for each molecule of the salt oxidised. Further convincing proof of the extent of oxidation by acid permanganate was the isolation of compounds of the type $R_3W(CN)_8$ from the oxidised solution of $K_4W(CN)_8$. Olsson was unsuccessful, however, in isolating the corresponding molybdenum type, $R_3Mo(CN)_8$. By taking special precautions, this has now been done, and not only have salts of this series been prepared, but also the complex *acid* $H_3Mo(CN)_8,3H_2O$ has been isolated. It is also hoped to show that a satisfactory explanation of the abnormal oxidation by acid permanganate is forthcoming from a consideration of the electronic theory of valency.

In researches on the complex cyanides of the type $R_4Mo(CN)_8$, Rosenheim and his co-workers (*Z. anorg. Chem.*, 1909, **65**, 166; 1907, **54**, 97) prepared derivatives where R was replaced by equivalent proportions of cadmium, thallium (univalent), manganese, pyridinium, and the ammines of silver, copper, and nickel. The methods of preparation and the compositions of the silver, copper, thallous, and ammino-silver compounds have been re-examined, confirming Rosenheim's data, whilst the isolation of the new insoluble, dark green *ammino-copper* salt, $[Cu(NH_3)_3]_2Mo(CN)_8$, and the dark blue, soluble *complex salt*, $[Cu\ en_2]_2Mo(CN)_8$, affords interesting examples of copper exhibiting co-ordination numbers of 3 and 4. In addition, a study of the so-called red and blue cyanides of quadrivalent molybdenum has been made, and a bright brick-red, insoluble compound, which is probably the complex acid $H[MoO_2(CN)_2,2H_2O]$, has been prepared by the action of concentrated nitric acid on $K_4Mo(CN)_8$.

Experimental.

Salts of the Type $R_4[Mo(CN)_8]$.—From the reaction of potassium cyanide with the complex chloride of tervalent molybdenum, K_3MoCl_6, Chilesotti (*Gazzetta*, 1904, **34**, ii, 493) obtained a yellow, crystalline salt of the composition $K_4Mo(CN)_8,2H_2O$, in which he assumed that the molybdenum was quadrivalent. The same

compound was isolated later by Rosenheim and Koss (*Z. anorg. Chem.*, 1906, **49**, 148) from the interaction of a derivative of quinquevalent molybdenum, $(NH_4)_2[MoOCl_5]$ or $Mo(OH)_2(CNS)_3(C_5H_5N)_2$, and potassium cyanide. Conductivity data (*ibid.*, 1907, **54**, 97) established that the ionisation was in accordance with the formula $K_4[Mo(CN)_8]$, whilst Collenberg (*ibid.*, 1922, **121**, 298) has confirmed Olsson's results, which indicated the quadrivalency of the central atom.

Tetrapotassium Molybdenum Octacyanide.—The method of Chilesotti (*loc. cit.*) was used. One part by weight of K_3MoCl_6 and 2 parts of potassium cyanide were intimately mixed and 6 parts of water added in small portions, during about 2 hours. The solution was raised to boiling point and concentrated on a water-bath, whereby yellow crystals were obtained. These were separated from the mother-liquor and extracted with small quantities of hot water, and the solution was filtered and allowed to crystallise. Further purification was obtained by redissolution in a little water and precipitation by alcohol with rapid stirring. The small, golden-yellow crystals thus prepared were very pure.

Analysis. It was found necessary to destroy the complex anion completely before the molybdenum could be precipitated quantitatively. The general method used was to digest the compound with boiling concentrated sulphuric acid for some time, dilute the mixture, make it alkaline with ammonia, and then add colourless ammonium sulphide solution and acid as previously described (J., 1924, **125**, 1911). Unfortunately, large quantities of ammonium sulphate have to be eliminated in the potassium estimation [Found : Mo, 19·2; K, 31·2; C, 19·3; N, 22·8. Calc. for $K_4Mo(CN)_8,2H_2O$: Mo, 19·4; K, 31·5; C, 19·4; N, 22·6%].

The compound, which is readily soluble in water, producing a yellow, slightly alkaline solution, is decomposed neither by dilute acids nor by alkalis. Concentrated sulphuric acid is required to effect complete decomposition. It is light-sensitive (Collenberg, *Z. anorg. Chem.*, 1924, **136**, 245), but not to such an extent as the analogous compound of quinquevalent molybdenum. A detailed account of its properties is given by Chilesotti (*loc. cit.*).

Tetrasilver Molybdenum Octacyanide.—Silver nitrate solution was added to a solution of $K_4Mo(CN)_8$, and the yellow silver salt which separated was washed with water and dried in a vacuum desiccator [Found : Ag, 58·3; Mo, 12·9. Calc. for $Ag_4Mo(CN)_8$: Ag, 58·7; Mo, 13·0%]. On being warmed with ammonia (*d* 0·88), this silver salt dissolved, and concentration of the solution over sulphuric acid yielded a yellow, crystalline compound insoluble in water. This was kept over concentrated sulphuric acid until free from the smell

of ammonia [Found: Ag, 54·5; Mo, 12·1; NH_3, 6·3. Calc. for $Ag_4(NH_3)_3Mo(CN)_8$: Ag, 54·8; Mo, 12·2; NH_3, 6·4%].

Tetrathallous Molybdenum Octacyanide.—This salt was prepared by adding the theoretical amount of a solution of thallous nitrate to a concentrated solution of $K_4Mo(CN)_8$, evaporating the mixture to small bulk, filtering, and allowing the salt to crystallise. The orange-yellow crystals obtained were washed with water and dried on a filter-paper.

Analysis. The substance was boiled with concentrated sulphuric acid until the solution was nearly colourless. On diluting it, making it alkaline with ammonia, and adding colourless ammonium sulphide solution, thallous sulphide was precipitated, which was washed with ammonium sulphide solution and filtered off. Molybdenum was estimated in the usual way in the filtrate and washings. The thallous sulphide was dissolved in dilute nitric acid, the solution evaporated to dryness, and potassium iodide added to an aqueous solution of the residue, precipitating thallous iodide, which was washed by decantation with potassium iodide solution, collected, and treated with alcohol to remove any potassium iodide [Found: Tl, 72·3; Mo, 8·6. Calc. for $Tl_4Mo(CN)_8$: Tl, 72·8; Mo, 8·5%].

The compositions of this salt and of the corresponding silver salt indicate that water of crystallisation, which is present in many of these complex cyanides, is not an essential constituent of the co-ordination complex.

Dicupric Molybdenum Octacyanide.—This was prepared by double decomposition of the potassium complex cyanide with copper sulphate solution. The precipitate was coagulated by boiling, washed with water, and dried in a vacuum desiccator; it was then dark purple.

Analysis. The substance was heated with concentrated sulphuric acid until a nearly colourless solution resulted; this was diluted and made just alkaline with sodium hydroxide, excess of sodium sulphide solution added, and the whole boiled for a few minutes to ensure all the molybdenum being present as the soluble thiomolybdate. The precipitated copper sulphide was filtered off, washed with sodium sulphide solution, then with hydrogen sulphide water, dried, and gently ignited. The residue, after being moistened with pure nitric acid and reheated, was weighed as copper oxide. The molybdenum in the filtrate and washings was precipitated as sulphide by the addition of dilute sulphuric acid, filtered off, and ignited to trioxide [Found: Mo, 22·1; Cu, 29·7. Calc. for $Cu_2Mo(CN)_8$: Mo, 22·3; Cu, 29·5%].

Hexamminodicupric Molybdenum Octacyanide.—By treatment of

the above copper salt with concentrated ammonia solution, Rosenheim (*Z. anorg. Chem.*, 1907, **54**, 97) obtained a dark green ammino-compound to which he assigned the formula $Cu_2(NH_3)_4Mo(CN)_8,7H_2O$. By the use of a similar method, a new *ammino-copper* derivative has been obtained. On addition of ammonia (*d* 0·88) to the purple $Cu_2Mo(CN)_8$, the colour changed to bright green. On warming, the solid dissolved, producing a dark green solution from which, after filtration and standing over sulphuric acid, dark green crystals separated, which were insoluble in water but could be recrystallised from ammonia solution (*ca.* 10*N*). The substance was washed with water and dried in a vacuum over sulphuric acid, whereupon the colour became a lighter green {Found: Mo, 17·8; Cu, 24·1; NH_3, 19·4. $[Cu(NH_3)_3]_2Mo(CN)_8$ requires Mo, 18·0; Cu, 23·9; NH_3, 19·1%}. Treatment with acid removes the ammonia and precipitates the purple $Cu_2Mo(CN)_8$.

Tetraethylenediaminodicupric Molybdenum Octacyanide.—The purple $Cu_2Mo(CN)_8$ (1 mol.) was mixed with ethylenediamine hydrate (4 mols.) and well shaken. A blue substance formed immediately and was recrystallised from water, in which it gave a deep bluish-purple solution. After being dried over sulphuric acid, the new salt was deep blue, readily soluble in warm water, and easily decomposed by dilute acids, $Cu_2Mo(CN)_8$ being precipitated {Found: Cu, 18·8; Mo, 14·3; N, 33·5. $[Cu(en)_2]_2Mo(CN)_8$ requires Cu, 19·0; Mo, 14·3; N, 33·4%}.

Conductivity measurements at 25° indicated, as would be expected from the formula, a maximum of 3 ions in very dilute solutions.

Dilution (litres per mol.)	155	310	620	1240
μ	78·5	104·3	134·4	166·2

For comparison, the values of the molecular conductivities of typical salts at 25° are given:

Dilution (litres per mol.)	128	256	512	1024
NaCl	113	115	117	118
K_2SO_4	246	257	265	273

In the more concentrated solutions, the molecular conductivity is even less than that required for a typical binary electrolyte, but at higher dilutions, although less than that demanded by a ternary electrolyte, it exceeds that of the binary electrolyte.

In the complex kations containing copper, it is possible to assign to the copper co-ordination numbers of 2, 3, and 4, but with the silver salt $[Ag_4(NH_3)_3]Mo(CN)_8$ it is difficult to discern any satisfactory co-ordination number for the silver atom.

Salts of the Type $R_3Mo(CN)_8$.—In attempting to isolate salts of this type, Olsson (*Ber.*, 1914, **47**, 917) added silver nitrate solution

to a solution of $K_4Mo(CN)_8$ which had been as fully oxidised as possible with acid permanganate. Thereby he obtained a reddish-brown precipitate obviously different from the yellow $Ag_4Mo(CN)_8$. By decomposition with potassium chloride solution, this reddish-brown silver salt gave a yellow liquid which could no longer be oxidised by permanganate. From this solution, green crystals of a copper salt were obtained, again distinct from the purple $Cu_2Mo(CN)_8$. The yellow liquid readily decomposed on warming or on exposure to light, yielding molybdic acid, hydrocyanic acid, and $K_4Mo(CN)_8$, and probably contained the salt $K_3Mo(CN)_8$. It appeared that this potassium salt could be satisfactorily isolated only in the absence of light.

Trisilver Molybdenum Octacyanide.—A solution of $K_4Mo(CN)_8$ was oxidised with acid permanganate until a faint pink colour remained. Excess of silver nitrate was then added, the resulting reddish-brown precipitate was washed repeatedly by decantation with water, and then dried in a vacuum. This substance was contaminated with manganese dioxide from the decomposition of the permanganate in the presence of the silver ions; by working with dilute solutions of both $K_4Mo(CN)_8$ and permanganate, however, the amount of dioxide produced was small. The reddish-brown precipitate was triturated with a little potassium chloride solution (insufficient for complete decomposition), and the yellow solution was filtered and again treated with silver nitrate solution. Any slight amount of chloride in the yellow solution is precipitated by the silver nitrate before the reddish-brown silver complex cyanide. Therefore, silver nitrate solution was carefully added until a faint brown precipitate was obtained, the solution again filtered, and the pure reddish-brown salt obtained by the addition of excess silver nitrate solution to the filtrate. The compound was washed with cold water and dried in a vacuum over phosphoric oxide.

Analysis. The silver was estimated as chloride by boiling the compound with concentrated sulphuric acid, diluting the solution, and adding either dilute hydrochloric acid or potassium chloride solution. The molybdenum was estimated in the usual way [Found: Ag, 51·3; Mo, 15·2; N, 17·6. $Ag_3Mo(CN)_8$ requires Ag, 51·6; Mo, 15·2; N, 17·7%].

Tripotassium Molybdenum Octacyanide. — The silver salt, $Ag_3Mo(CN)_8$, was triturated with insufficient potassium chloride solution for complete decomposition. The filtered yellow solution, which contained no chloride, was concentrated in a vacuum desiccator over phosphoric oxide, whereupon yellow needles were obtained. These operations were carried out in a dark room with a

red light, and the solid was preserved in a desiccator covered with black paper. In daylight, the yellow crystals turned reddish-brown [Found: Mo, 22·4; N, 26·4; K, 28·2. $K_3Mo(CN)_8$ requires Mo, 22·8; N, 26·6; K, 27·8%]. Because of its sensitivity to light, conductivity measurements were not carried out on the new complex cyanide. By addition of copper sulphate solution to the yellow solution of the new salt, a grass-green precipitate was obtained, which, after a few minutes' exposure to light, turned purple.

Trihydrogen Molybdenum Octacyanide.—The yellow solution, produced by triturating the complex silver salt with a little dilute hydrochloric acid and filtering, was saturated with hydrogen chloride at the temperature of an ice–salt mixture. A reddish-orange substance separated, which was possibly an addition compound of hydrogen chloride with the required complex acid. This was filtered off and dried in a vacuum over potassium hydroxide and phosphoric oxide, and thereby became orange-coloured and free from hydrogen chloride. The new solid gave a yellow, aqueous solution, from which silver and copper salts precipitated the characteristically coloured complex cyanides of quinquevalent molybdenum. The same compound is obtained if the yellow solution is concentrated in a vacuum over potassium hydroxide and phosphoric oxide, without saturation with hydrogen chloride. In either case, all operations must be conducted in the absence of light. The new *acid* is extremely deliquescent [Found: Mo, 26·7; N, 31·1. $H_3Mo(CN)_8,3H_2O$ requires Mo, 26·6; N, 31·0%].

In order to confirm the constitution of the substance and to demonstrate its freedom from hydrogen chloride, a solution of the complex acid was treated with silver nitrate solution, all the molybdenum being thereby precipitated as $Ag_3Mo(CN)_8$. This precipitate was washed free from silver nitrate, and excess of potassium chloride solution added. The $Ag_3Mo(CN)_8$ was thereby converted quantitatively into silver chloride, which was washed and weighed. Any hydrogen chloride in the original substance would also have been precipitated as silver chloride. 0·2164 G. of the new acid, containing 26·7% of Mo, gave 0·2606 g. of AgCl; hence Mo : AgCl = 1 : 3·02, proving also the absence of hydrogen chloride from the complex acid.

The Abnormal Oxidation of the Complex Cyanides.

On the basis of the electronic theory of valency, an explanation is now available of the abnormal behaviour of the complex cyanides of molybdenum on oxidation with acid permanganate. Estimation of the valency of the molybdenum in $K_4Mo(CN)_8$ through titration with acid permanganate involves the consumption of only one equi-

valent of oxygen for each molecule of salt oxidised, from which one would conclude that the molybdenum was quinquevalent, since the usual end-product would be expected to contain sexavalent molybdenum. This, however, does not agree with the formula of the compound, in which the molybdenum must be quadrivalent. That, by complete oxidation with acid permanganate, the molybdenum in $K_4Mo(CN)_8$ is oxidised from the quadrivalent to the quinquevalent condition, is now clearly shown by the isolation of the complex salts $R_3Mo(CN)_8$ from the fully oxidised solution of $K_4Mo(CN)_8$. Ephraim ("Inorganic Chemistry," English transl., 1926, p. 280), commenting on this exceptional oxidation, says: "It is not easy to see the explanation of this anomaly, but it is possible that the metal atom is surrounded by voluminous radicles which are fairly firmly attached." A much more satisfactory explanation is forthcoming from a consideration of the effective atomic number of the central atom in the various complex salts involved in the preparation of the complex cyanides. The salt $K_4Mo(CN)_8$ is normally prepared by the interaction of potassium cyanide with complex compounds of either tervalent or quinquevalent molybdenum. In the former case the reaction may be conveniently formulated as $K_3MoCl_6 + 8KCN + \frac{1}{2}H_2O + \frac{1}{2}O(air) = K_4Mo(CN)_8 + 6KCl + KOH$. The instability of the intermediate $K_3Mo(CN)_6$—a salt as yet unisolated—which reverts to the stable $K_4Mo(CN)_8$, can be readily appreciated when it is seen that the effective atomic number of the molybdenum is only 51, whereas in the stable compound it is 54. In the preparation from the complex chlorides of quinquevalent molybdenum, R_2MoOCl_5, the importance of the effective atomic number of the molybdenum in $K_4Mo(CN)_8$ is again emphasised. The reaction may be considered as occurring in the following stages :

$$K_2MoOCl_5 + 5KCN = K_2MoO(CN)_5 + 5KCl$$
$$K_2MoO(CN)_5 + 3KCN + H_2O = K_3Mo(CN)_8 + 2KOH$$
$$2K_3Mo(CN)_8 + 2KOH = 2K_4Mo(CN)_8 + H_2O + \tfrac{1}{2}O_2$$
$$[\text{compare } 2K_3Fe(CN)_6 + 2KOH = 2K_4Fe(CN)_6 + H_2O + \tfrac{1}{2}O_2]$$

The instability of the salt $K_2MoO(CN)_5$ follows as a consequence of the low effective atomic number, *viz.*, 49, of the molybdenum atom, whilst the formation of $K_4Mo(CN)_8$ from $K_3Mo(CN)_8$ involves a change of an effective atomic number of 53 to 54—a clear proof of the influence of an inert-gas structure in determining chemical stability. The inability to oxidise $K_4Mo(CN)_8$ to the salt $K_2Mo(CN)_8$ of sexavalent molybdenum, with an effective atomic number of 52, is not surprising in view of the experimental evidence that $K_3Mo(CN)_8$ functions as an oxidising agent in order to revert to

the more stable $K_4Mo(CN)_8$. This change, as has been previously mentioned, is readily brought about by light or by the action of heat. Further evidence of the instability of the system $[Mo(CN)_8]'''$ is seen in the rapidity with which, in light, the green complex salt $Cu_3[Mo(CN)_8]_2$ reverts to the purple $Cu_2[Mo(CN)_8]$. Oxidation to the sexavalent condition is realised only by complete decomposition of the complex anion. When the complex salt $K_4Mo(CN)_8$ is oxidised by ammoniacal silver nitrate, the molybdenum is converted into the trioxide.

The Red and the Blue Cyanides of Quadrivalent Molybdenum.

Just as the yellow cyanide, $K_4Mo(CN)_8$, results from the reaction of potassium cyanide with salts of tervalent and quinquevalent molybdenum, so by adjusting the proportion of the reactants so that 1 g.-mol. of the salt of quinquevalent molybdenum reacts with 4 g.-mols. of potassium cyanide, a red cyanide is obtained, which may be formulated as either $[Mo(OH)_4(CN)_4]K_4,xH_2O$ or $[MoO_2(CN)_4]K_4,(x + 2)H_2O$. Moreover, by use of excess potassium cyanide the red will revert to the yellow salt in accordance with the equations

$$[Mo(OH)_4(CN)_4]R_4 + 4RCN = [Mo(CN)_8]R_4 + 4ROH,$$
$$[MoO_2(CN)_4]R_4 + 4RCN = [Mo(CN)_8]R_4 + 2R_2O.$$

By strong dehydration over sulphuric acid, or by cautious heating, these red cyanides become blue; their aqueous solutions also are blue. Addition of potassium hydroxide in sufficient concentration to the blue aqueous solution results in the reprecipitation of the red cyanide. The addition of alcohol to the blue aqueous solution causes the precipitation of a blue solid, which, after being dissolved in water and reprecipitated several times, has a composition for which various formulæ have been proposed. Two in particular may be noted: $MoO_2,4KCN,5H_2O$ and $Mo(OH)_2(CN)_2,3KCN$. These show the quadrivalency of the molybdenum, but indicate the possibility that quite different blue complex cyanides exist. With the object of investigating the reasons for these striking colour changes, samples of the red and the blue cyanides were prepared and examined.

The Red Cyanides.—By the reduction of an acid solution of molybdenum trioxide with potassium iodide, removal of the excess iodine, and subsequent treatment with potassium cyanide and hydroxide, Heide and Hofmann (*Z. anorg. Chem.*, 1896, **12**, 277) obtained red crystals to which they assigned the formula

$$4KCN,MoO_2,10H_2O.$$

Rosenheim, Garfunkel, and Kohn (*ibid.*, 1910, **65**, 166) obtained a similar compound by treating $(NH_4)_2MoOCl_5$ or

$$Mo(OH)_2(CNS)_3(C_5H_5N)_2$$

—salts of quinquevalent molybdenum—with potassium cyanide, and subsequently adding potassium hydroxide. The method used by the present authors followed that of Péchard (*Compt. rend.*, 1894, **118**, 804), who dissolved molybdenum pentoxide in potassium cyanide solution, and precipitated the red crystals by the addition of solid potassium hydroxide to the blue solution.

300 C.c. of a solution of molybdenum trioxide (10%) in hydrochloric acid (3*N*) were electrolysed in a diaphragm cell for 2 hours (1 amp.; 8 volts) and concentrated at *ca.* 70° to a very small bulk. On careful addition of very concentrated potassium hydroxide solution, the brown hydroxide of quinquevalent molybdenum was obtained. On addition of the theoretical amount of potassium cyanide (54 g.) as a saturated solution, the hydroxide slowly dissolved, producing a blue solution, which was filtered and concentrated under diminished pressure at *ca.* 70° to a small bulk (30—40 c.c.). Red crystals were deposited on addition of solid potassium hydroxide to this blue solution. By means of a little water and then alcohol, the crystals were freed from potassium hydroxide. They are stable towards dilute mineral acids, but appear to be decomposed by organic acids, such as salicylic or oxalic acid, although no definite compounds could be obtained. In the presence of concentrated potassium hydroxide, the crystals exhibit a bright red colour, but as the hydroxide is removed the colour becomes bluish-red.

Analysis. An aqueous solution of the substance was oxidised with hydrogen peroxide and made alkaline with ammonia, and colourless ammonium sulphide was added. Addition of dilute sulphuric acid precipitated the molybdenum as sulphide, which was ignited and weighed as trioxide. The potassium in the filtrate was weighed as sulphate {Found : Mo, 19·3; K, 31·1; C, 9·9; H, 2·4; N, 11·5. Calc. for $K_4[Mo(OH)_4(CN)_4],4H_2O$: Mo, 19·3; K, 31·4; C, 9·6; H, 2·4; N, 11·3%}.

Even when the crystals did not contain any free potassium hydroxide, their aqueous solution gave an alkaline reaction with phenolphthalein, suggesting hydrolysis. This view is supported by the conductivity data, which indicate that, even at 1°, more than 5 ions are present in dilute solutions. The table gives the value of μ for various dilutions v (as litres per mol.).

v	23·5	47	94	188
μ	275·6	298·4	320·6	342·3

(compare this vol., p. 516, Table IV, for conductivities of typical salts at 1°).

Molecular-weight Determinations.—The molecular weight was determined by the depression of the freezing point of air-free water.

G. of substance per 100 g. water.	Conc. (mol. per 1000 g. water).	Osmotic factor.	Apparent mol. wt.
0·7136	0·01440	5·16	96·2
1·517	0·03560	5·06	97·9
2·636	0·05314	4·85	102·6

These results indicate the correctness of a formulation which requires 5 ions, but they also show that slow hydrolysis takes place in dilute aqueous solution.

The Blue Cyanides.—An aqueous solution of the red cyanide was treated with alcohol, whereby a blue precipitate resulted. The mother-liquor was alkaline to phenolphthalein, indicating that by the conversion of the red into the blue cyanide, potassium hydroxide was removed. The blue solid was redissolved in water and re-precipitated with alcohol; these operations were repeated until the mother-liquor from the precipitation was no longer alkaline. Thereby a blue substance was obtained {Found: Mo, 22·5; K, 28·0; C, 11·5; N, 13·1. $K_3[Mo(OH)_3(CN)_4,H_2O],2H_2O$ requires Mo, 22·7; K, 27·8; C, 11·3; N, 13·3%}.

The aqueous solution of this compound was alkaline to phenolphthalein, and with potassium cyanide yielded the yellow $K_4Mo(CN)_8$. The blue substance was prepared several times by the above method and always had the same composition. The formulation given above was in accordance with the results of molecular-weight and conductivity determinations, which indicated that 4 ions were present in solution but that gradual hydrolysis also took place.

Molecular-weight Determinations.

G. of substance per 100 g. water.	Conc. (mol. per 1000 g. water).	Osmotic factor.	Apparent mol. wt.
0·6618	0·01554	4·25	99·3
1·235	0·02898	4·23	99·7

Molecular-conductivity Determinations, at 1°.

v	35·5	71	142	284
μ	198·8	215·5	232·8	250·0

The Relationship of the Red and the Blue Cyanides.—The fact that the red cyanide becomes blue on dehydration and yet yields a blue aqueous solution seems to depend on the equilibrium

$$K_4[Mo(OH)_4(CN)_4],4H_2O \rightleftharpoons K_3[Mo(OH)_3(CN)_4,H_2O],2H_2O + KOH + H_2O.$$

It was noticed that the red colour of the complex cyanide is attained only in the presence of concentrated potassium hydroxide, and that on removal of this free alkali the pure complex salt becomes bluish-violet. It appears probable, therefore, that on dehydration and on dissolution in water, a decomposition takes place in accordance with the above equation. A co-ordination number of 8 for

the molybdenum atom in the red cyanides seems indicated by the fact that on cautious dehydration over sulphuric acid or at 100° they retain 2 mols. of the associated water, suggesting the formula $R_4[MoO_2(CN)_4,2H_2O]aq.$ or $R_4[Mo(OH)_4(CN)_4]aq.$

Brick-red, Insoluble Molybdenum Cyanide.—Chilesotti (*Gazzetta*, 1904, **34**, ii, 493) noticed that the oxidation of the yellow quadrivalent cyanide by means of concentrated nitric acid resulted in the separation of a brick-red, insoluble compound, which he did not further examine.

When $K_4Mo(CN)_8$ was heated with even dilute nitric acid (*ca.* 6*N*) in a test-tube, this compound was obtained pure, but when the experiment was made in an open dish, varying amounts of molybdic acid were formed. The brick-red compound was washed with cold water, in which it was but slightly soluble, and dried in a desiccator over sulphuric acid.

Analysis. The substance was heated with pure sulphuric acid until the solution was colourless, and the molybdenum precipitated as previously described {Found : Mo, 43·8; N, 12·8; C, 11·0; H, 1·8. $H[MoO_2(CN)_2,2H_2O]$ requires Mo, 44·2; N, 12·9; C, 11·0; H, 2·3%}.

Valency. A solution of the substance in dilute aqueous ammonia was made acid with sulphuric acid and titrated with permanganate. On the assumption that the molybdenum in the compound has a valency of 5, the theoretical content of molybdenum calculated from the titration is 44·8%. By gravimetric means it was found to be 43·8%. Hence the molybdenum is quinquevalent.

The solid is soluble in hot water, giving a yellow solution. It is much more readily soluble in ammonia or alkalis, suggesting an acidic structure. In view of this, it is probably correctly formulated as above.

This new derivative is of interest as indicating that on oxidation the quinquevalent molybdenum still persists as a complex anion, but that on oxidation to the sexavalent state complete disruption of the complex ion takes place, a fact which is in complete agreement with the theoretical considerations previously advanced to explain the abnormal oxidation of the yellow complex cyanides.

The authors wish to express their thanks to the Department of Scientific and Industrial Research for the award of a grant to one of them (W. R. B.), and to the Chemical Society and the University of Birmingham Research Committee for grants in aid of this investigation.

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CCCXCVIII.—*Equilibrium Diagram of the System Thallium–Phosphorus.*

By Qasim Ali Mansuri.

The system thallium–phosphorus has not hitherto been investigated. Thallium was prepared as previously described by the author (*J. Inst. Metals*, 1922, **28**, 453); its purity was 99·5%, the chief impurity being iron (less than 0·3%). Merck's pure red phosphorus was repeatedly boiled with water and then showed a content of 99·91%.

Preparation of Alloys.—Molten thallium alloyed readily with phosphorus, and the action was more marked above 400°. When more than 2·5% of phosphorus had been added, the alloys separated into two layers, the upper one being dark and brittle, and the lower layer soft. The dark substance was readily oxidised to phosphoric acid on being exposed to the air.

Thermal Analysis.—To avoid oxidation of the mixtures, they were prepared in hard-glass tubes from weighed quantities of thallium or the alloy and not more than 1 g. of free phosphorus at a time. The tubes were then evacuated and sealed and the cooling curves were obtained by applying the hot junction of a nichrome–constantan couple to the outside of the tube, contact being made more intimate by means of fireclay. The tubes were packed in sand in an iron tube about 1½ inches in diameter and 1 foot in length, the whole being heated in an electrical tube furnace. The molten alloy was thoroughly mixed by repeatedly tilting the furnace, and the cooling curves were then taken.

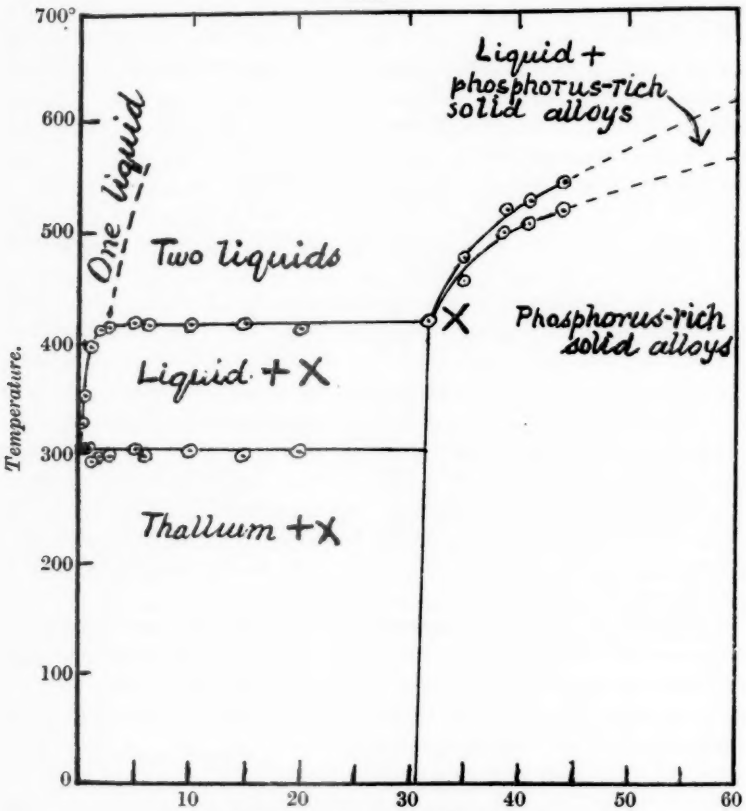
A suspended mirror galvanometer and scale were used for taking temperatures, the rate of cooling being about 8° per minute at high temperatures and about 5° per minute below 300°. Half-minute readings gave the following thermal arrests from which the equilibrium diagram was constructed.

Alloy No.	P, % by weight.	Thermal arrests. 1.	2.	Alloy No.	P, % by weight.	Thermal arrests. 1.	2.
1	0·00	—	303°	9	10·00	416°	303°
2	0·17	328°	302	10	15·00	418	298
3	0·38	352	303	11	20·00	412	300
4	0·87	396	290	12	31·40	420	—
5	2·00	410	296	13	35·00	476	456
6	2·50	412	296	14	38·75	520	500
7	5·00	418	302	15	41·20	528	506
8	6·08	416	296	16	43·90	546	520

Alloys containing from 2·5% to about 27% of phosphorus show two layers, the lower layer being practically pure thallium and

freezing at the melting point of that metal. Thallium, therefore, does not seem to dissolve any of the upper layer at its melting point. The upper layer freezes at about 420°. In alloys containing more than 2·5% of phosphorus, the two layers may dissolve in each other at higher temperatures than 420°. An attempt was made to find at what temperatures the two layers dissolved in each other

FIG. 1.



Equilibrium diagram of the system thallium–phosphorus.

by heating the alloys to definite temperatures above 420° and chilling them, but a considerable pressure was developed and the tubes burst. However, an alloy containing about 0·2% of phosphorus was heated to 350° and chilled; although this burst in water, a small piece was obtained which, on being polished, was found to be uniform, showing that in this alloy the two layers were miscible at about 350°. The solubility of the two layers in each other is there-

fore dependent upon the temperature. A short dotted line has been drawn on the left side of the diagram to indicate this solubility.

Composition of the Alloys.—As most of the alloys were not homogeneous, they were not analysed, but their compositions were deduced from the weights of the constituents in the tubes. The upper dark layer, which was brittle, could be separated by powdering; it contained 31·4—31·5% of phosphorus. The lower layer contained no phosphorus. The thallium was estimated as described by the author (*loc. cit.*), and the quantity of phosphorus was found by difference.

Conclusions.

1. Up to 45% of phosphorus, thallium and phosphorus alloy in all proportions.

2. They form a homogeneous substance, X, containing about 31·4% of phosphorus and melting at about 420°. At this temperature, about 8% of this substance dissolves in thallium, to give an alloy containing 2·5% of phosphorus. Owing to the low solubility of X in thallium, the alloys separate into two layers, the upper layer being X and the lower layer a solution of a small quantity of X in thallium. On cooling, thallium gradually loses all the X dissolved in it and freezes at its melting point.

3. Quantities of phosphorus in excess of 31·4% dissolve in X and form solid solutions, which freeze at temperatures above 420° and over a temperature range. The phosphorus may exist as yellow phosphorus in these alloys, for they take fire when rubbed on emery paper.

4. The substance X tends to dissociate into its constituents at all temperatures, and a high pressure is therefore necessary for its formation; owing to this high pressure, the solubility curve of X in thallium could not be studied.

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CCCXCIX.—*An Auto-poisoning Phenomenon shown by Catalytically Active Copper at Moderate Temperatures.*

By FREDERICK HURN CONSTABLE.

THE author has previously shown (this vol., p. 1578) the extent to which sintering by heat treatment reduces the surface area and catalytic activity of copper, and has also provided definite evidence that the " centres of activity " collapse when the kinetic energy of the constituent atoms becomes sufficient. The heterogeneous nature

of the active surface is now well recognised, and the present paper shows how the active centres may be rendered inactive during the catalysis of a chemical change, even when precautions are taken that the reactant is quite pure, and that the temperatures are below those at which sintering of the centres occurs in a vacuum, in spite of the fact that the reaction proceeds with the absorption of heat.

When a copper catalyst is used to dehydrogenate alcoholic substances at temperatures above 280°, it is found that the activity decays with time. Measurements have been made on the variation of activity with time, and on the effect of temperature on the rate of decay. The catalyst is stable when heated alone to the temperature used, so the poisoning is due to the interaction of the copper and the alcohol. It has been shown that the method of preparation of the catalyst does not alter the temperature at which the effect becomes noticeable, though it seems to have a considerable influence on the rate of poisoning, the rate of decay of the preparation from copper oxalate being about 5 times greater than that of copper reduced from oxide at the same temperature (*Proc. Roy. Soc.*, 1926, *A*, **110**, 297, Fig. 2, curve 5, and Fig. 5).

Experimental.

The ethyl alcohol was twice refluxed with lime, distilled through a Dufton column, and collected in a receiver fitted with a phosphorus pentoxide guard tube; it had b. p. 78·30° ± 0·01°/760 mm. The apparatus used has already been described (*Proc. Camb. Phil. Soc.*, 1925, **22**, 739). The initial stages of the reaction were always studied, and the rate of flow of the alcohol was regulated so that the concentration of the aldehyde over the catalyst was never greater than 1%. The amount of copper used as a catalyst had to be decreased as the temperature of experiment was increased. The rate of poisoning at constant temperature is not dependent on the rate of passage of the alcohol vapour when this exceeds a definite limiting value, and is therefore not dependent on the small concentration of the aldehyde in the vapour above the catalyst.

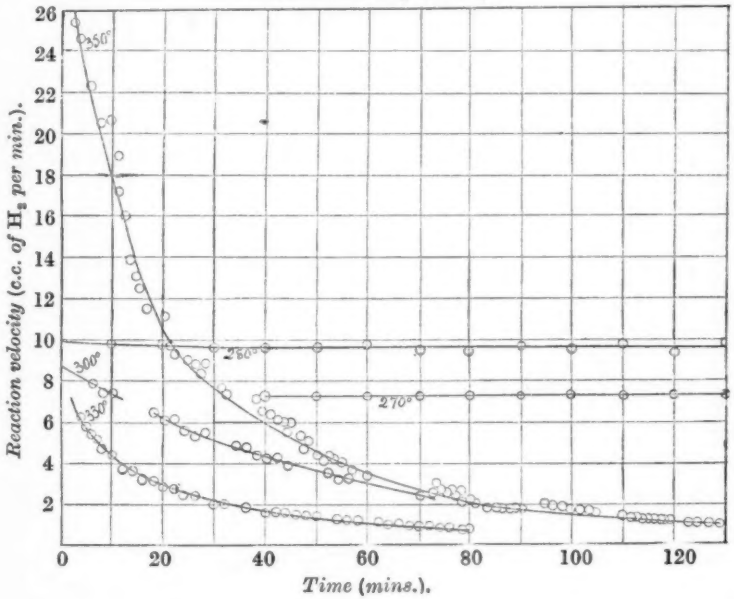
The reaction tube was filled with carbon monoxide at the constant temperature at which the decay of activity was to be measured, and the copper oxide thereby reduced. Blank experiments were made with water vapour instead of alcohol in order to determine the magnitude of the correction which had to be applied on account of the displacement of carbon monoxide from the reaction tube in the initial stages of the reaction. The correction was very large in the first few minutes after the bulk of the gas had suddenly been displaced by the admission of the vapour stream. It was found that a current of steam produced by the vaporisation of 1·28 c.c. of water

per minute would take about 10 seconds to pass the glass valve B_2 (*Proc. Camb. Phil. Soc., loc. cit.*, Fig. 1), and during this time the valve condensed the gas stream and was being warmed; then followed a very rapid evolution of gas from the reaction tube, lasting about 25 seconds, which stopped suddenly when the vapour stream reached the condenser K. The gas which had escaped removal by diffusion was then evolved at a continually decreasing rate, which was carefully measured; the readings so obtained are in Table I,

FIG. 1.

Decay curves at 270—350°.

(The catalyst was produced by reduction at the temperature of experiment, the amount being varied.)



the time from the commencement being given in minutes, and the rate of evolution in c.c. per minute. This correction was applied to

TABLE I.

Time	5	10	15	20	25	30	35
Rate	0·80	0·45	0·33	0·30	0·22	0·20	0·18

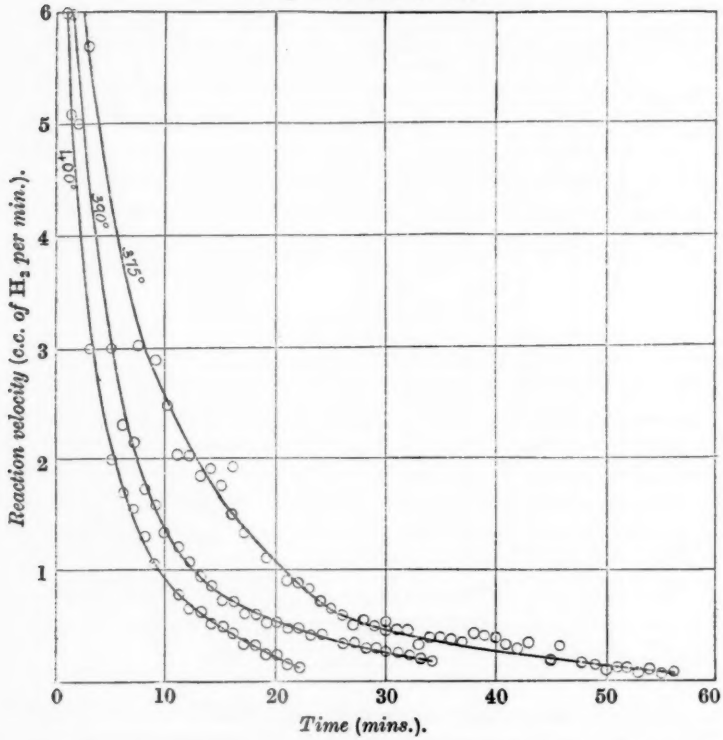
all the measurements made, but owing to variations in this quantity with the rate of flow the magnitude of the correction in the period 0—5 minutes is subject to considerable uncertainty. The measurements are thus somewhat untrustworthy except when the reaction

velocity is large, and if the activity is short-lived the precise form of the curve may be doubtful, *e.g.*, at 400°.

Procedure.—The alcohol stream was turned on, and 20 seconds were allowed for the time taken by the gas stream to reach the copper, and hence for the commencement of the reaction. The gas burette T was read every 30 seconds in the first 5 minutes, and then every minute until the activity became inappreciable. The corrected

FIG. 2.

Decay curves at 375—400°.



results of the experiments are shown in Figs. 1 and 2, and the fractional reaction velocities during each decay are given with the corresponding temperatures in Fig. 3. The value of the initial activity was obtained by extrapolation of the measurements in the very early stages of the poisoning.

Examination shows that the data follow neither a simple logarithmic law nor a reciprocal law. The initial logarithmic rate of decay, $d \log v/dt = 1/v \,.\, (dv/dt)$, is considerably retarded as the time proceeds. One typical set of observations at 350° is given in Table II,

TABLE II.

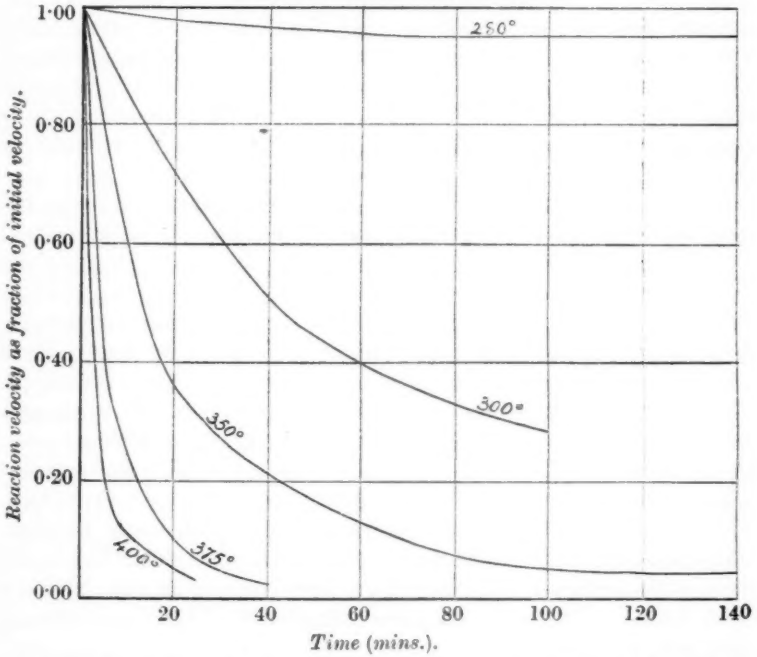
Time	0	10	20	30	40	50	60
Velocity	29·0	18·0	10·7	8·3	6·6	4·8	3·6
Time	70	80	90	100	110	120	130
Velocity	2·7	2·0	1·8	1·5	1·3	1·1	1·0

the time being in minutes, and the reaction velocity in c.c. of hydrogen (reduced to *N.T.P.*) evolved per minute.

It is thought that these data may represent a particular case of the selective poisoning of a distribution of centres of activity, and the

FIG. 3.

The fractional reaction velocities.



question is still under investigation. In the absence of definite knowledge of the law of decay, the time required for the velocity five minutes after the commencement to fall to one-tenth of its value has been used as a measure of the rate of poisoning at various temperatures; these times (in mins.), as read from the curves, are shown in Table III.

TABLE III.

Variation of Rate of Poisoning with Temperature.

Temp.	280°	300°	330°	350°	375°	390°	400°
Time	Very large	200	90	65	30	25	13

The rate of poisoning increases rapidly with the temperature, and is so fast that it can hardly be observed above 400°.

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CAMBRIDGE. [*Received, November 8th*, 1927.]

CCCC.—*Substitution Products of 3-Nitro- and 3-Amino-diphenyl.*

By WILLIAM BLAKEY and HAROLD ARCHIBALD SCARBOROUGH.

THE study of the orientation of substituents in 2-amino- and in 4-amino-diphenyl and in their acetyl derivatives (J., 1926, 557; this vol., pp. 89, 1133) has now been extended to a consideration of the substitution products of 3-nitro- and of 3-amino-diphenyl. The inclusion of 3-nitrodiphenyl in the scope of the work makes it possible to compare the behaviour of the three possible mononitrodiphenyls as well as the three monoaminodiphenyls.

The chlorination of 3-nitrodiphenyl took place readily in the presence of a powerful catalyst and at moderately high temperatures. The product was a mixture of compounds, containing one to four atoms of chlorine per molecule, the composition of which depended on the temperature and the duration of the chlorination. From these mixtures, *4′-chloro-*, *2′ : 4′-dichloro-*, a *tri-* and a *tetrachloro-3-nitrodiphenyl* were isolated. Isomeric mono- and dichlorination products could not be isolated from the semi-solid matter deposited on slow evaporation of the crystallising media. A structure has not been assigned to the higher chlorination products, although the evidence indicated that 2′ : 4′ : 5-trichloro- and 2′ : 4′ : 5 : 6′-tetrachloro-3-nitrodiphenyl had been isolated. The possibility that a chlorine atom was substituted in the 2-, 4-, or 6-position seems to be excluded, since piperidine did not react with either of these compounds (compare Le Fèvre and Turner, this vol., p. 1113).

3-Nitrodiphenyl on bromination yielded *4′-bromo-3-nitrodiphenyl* as the sole product. The introduction of a second bromine atom could not be effected under the most drastic conditions.

The nitration of 3-nitrodiphenyl in fuming nitric acid solution yielded a mixture of 3 : 4′- and 2′ : 3-dinitrodiphenyl. Further nitration, in sulphuric acid solution, of each of these isomerides led to the same product; and since this product on treatment with piperidine yielded 2′ : 3 : 4′-trinitro-4-piperidinodiphenyl (Le Fèvre and Turner, J., 1926, 2041), it must have the structure 2′ : 3 : 4 : 4′-*tetranitrodiphenyl*. Attempts were made to prepare a trinitrodi-

phenyl, but the product proved to be a mixture which could not be separated into its constituents.

The direct chlorination of 3-aminodiphenyl in glacial acetic acid and in carbon tetrachloride solution gave black, resinous masses which were not further investigated. 3-Acetamidodiphenyl, however, gave a stable N-*chloroamine* which could be converted, on treatment with alcohol and acetic acid, into 4-chloro-3-acetamidodiphenyl. The same product was obtained by direct chlorination of 3-acetamidodiphenyl in glacial acetic acid solution. An unstable *N*-chloroamine was obtained by treating 4-chloro-3-acetamidodiphenyl with sodium hypochlorite; the evolution of free chlorine from this compound may be taken as an indication that a second chlorine atom cannot be introduced into either nucleus by the indirect method.

Bromination of the free base in carbon tetrachloride solution yielded 4-*bromo*-3-*aminodiphenyl hydrobromide* and after prolonged treatment 2 : 4 : 6-*tribromo*-3-*aminodiphenyl*. In acetic acid solution bromination of the free base gave a quantitative yield of 2 : 4 : 6-*tribromo*-3-*aminodiphenyl*. Under the usual experimental conditions, 3-acetamidodiphenyl did not yield an *N*-bromoamine. Direct bromination of the acetyl derivative in glacial acetic acid solution at the ordinary temperature gave a nearly quantitative yield of 4-*bromo*-3-*acetamidodiphenyl*; in the presence of excess bromine and at 100—120°, 4 : 6-*dibromo*-3-*acetamidodiphenyl* was obtained. Higher bromination products did not appear to be formed.

On nitration of 3-acetamidodiphenyl in a mixture of glacial acetic acid and acetic anhydride at 70°, 4-*nitro*-3-*acetamidodiphenyl* was isolated in an approximately 50% yield; the residue was a viscid oil from which a crystalline compound could not be obtained. Nitration of 3-acetamidodiphenyl and of 4-bromo-3-acetamidodiphenyl in fuming nitric acid solution yielded 4′-*nitro*-3-*acetamidodiphenyl* and 4-*bromo*-4′-*nitro*-3-*acetamidodiphenyl*, respectively.

A comparison of the results obtained on the introduction of a further substituent into the isomeric mononitrodiphenyls shows that there is a great similarity of behaviour. Thus in each case further substitution takes place in the 2′- or the 4′-position of the unsubstituted nucleus. Bromination yields one product only, the bromine atom entering the 4′-position, and further bromination cannot be effected (compare Turner and Le Fèvre, J., 1926, 2041). The nitration of each of the isomerides yields two dinitrodiphenyls, the entering group substituting in the 2′- or the 4′-position. The relative proportion in which these isomerides are formed appears to vary with the position of the nitro-group originally present, since

3-nitrodiphenyl yields a much higher percentage of a product substituted in the 4′-position than does 4-nitrodiphenyl (compare Bell and Kenyon, J., 1926, 2705). The formation of 2′ : 3 : 4 : 4′-*tetranitrodiphenyl*, in almost quantitative yield, by the further nitration of 2′ : 3- and of 3 : 4′-dinitrodiphenyl is of considerable interest, since compounds having this orientation of their substituents may be obtained from widely different starting points; thus 4-bromo-2′-nitro-, 4-bromo-4′-nitro-, and 4 : 4′-dibromo-diphenyl yield products of this type on nitration.

A comparison of the substitution products of the isomeric monoaminodiphenyls shows that bromination can be carried out progressively until each position in the *op*-relationship to the amino-group has been substituted. The *p*-position to the amino-group is not necessarily the first position to be attacked, as will be seen from a comparison of 2- and 3-aminodiphenyl.

The acetyl derivatives of the three bases form stable *N*-chloroamines which may be converted into nuclear-substituted compounds, but in each case one chlorine atom only may be introduced by this method. Direct halogenation of the acetyl derivatives cannot be carried as far as in the case of the free bases, one position in the ring containing the acetamido-group resisting substitution.

The product isolated on nitration of any of the acetyl derivatives in fuming nitric acid solution or in solution in a strong mineral acid is one substituted in the 4′-position, whereas the product isolated on nitration in acetic acid solution is one substituted in the ring containing the acetamido-group.

4-Acetamidodiphenyl appears to differ from its isomerides in that bromination in the 4′-position can take place without previous substitution in the 3-position.

In a previous communication (J., 1926, 557), tentative rules for the orientation of substituents in the diphenyl series were proposed. The increased data now available show that but little modification of those rules is needed. It was assumed that the linkage between the two nuclei of diphenyl was of such a nature that either phenyl group, like all other hydrocarbon residues, acted as a negative (*op*-directive) group. It now seems well established that the directive power of the phenyl group is appreciably less than that due to the acetamido-group, but is greater than that due to chlorine or bromine.

The directive power of the groups C_6H_4X and C_6H_3XY depends on the nature of the substituents X and Y: when X or Y inhibits further substitution in the nucleus in which it occurs, the directive power of the group as a whole will be decreased, and this decrease becomes more marked when X or Y is a positive group.

EXPERIMENTAL.

3-Nitrodiphenyl.—Bamberger's method (*Ber.*, 1896, **29**, 446; see also Jacobsen, *Ber.*, 1903, **36**, 4083; Gomberg, *J. Amer. Chem. Soc.*, 1924, **46**, 2339; 1926, **48**, 1372), slightly modified, was found to be the most economical for the preparation in bulk. A paste of 50 g. of *m*-nitroaniline and 80 c.c. of concentrated hydrochloric acid was treated with a solution of 35 g. of sodium nitrite in 100 c.c. of water. Frothing was diminished by the addition of thiophen-free benzene, the volume of which was made up to 300 c.c. on completion of the reaction. This mixture was made alkaline with a 15% solution of sodium hydroxide (*ca.* 300 c.c., added drop by drop) and then acidified with glacial acetic acid. The whole series of operations was carried out below 5° and with vigorous stirring. The semi-solid mass was heated on the water-bath for 30 minutes, the sodium acetate removed, and the benzene layer separated from the aqueous layer and treated with benzene–light petroleum (b. p. 40—60°) to precipitate tar. The clear liquid was decanted, concentrated to about one-tenth of its bulk, and treated with light petroleum so long as tar separated. The clear liquid was decanted, washed with dilute sodium hydroxide solution and with water, and dried over fused sodium sulphate. The sodium acetate and the tars were boiled with light petroleum, and the extract was worked up in the same manner as for the main yield. The 3-nitrodiphenyl crystallised from alcohol in pale yellow needles (yield, 10—12 g.), m. p. 62°.

4′-Chloro-3-nitrodiphenyl was prepared by passing dry chlorine into a mixture of 10 g. of 3-nitrodiphenyl and 1 g. of ferric chloride, heated at 80°, until the gain in weight was 2 g.; or by passing chlorine into a 10% solution of 3-nitrodiphenyl in carbon tetrachloride in the presence of a trace of iodine and keeping the solution for several days. The product after repeated crystallisations from methyl alcohol separated in fine, white needles, m. p. 89° (Found: Cl, 14·9. $C_{12}H_8O_2NCl$ requires Cl, 15·2%).

4′-Chloro-3-acetamidodiphenyl.—5 G. of 4′-chloro-3-nitrodiphenyl in 50 c.c. of alcohol were refluxed with 25 g. of stannous chloride in 25 c.c. of concentrated hydrochloric acid for 6 hours and the mixture was then cooled and rendered alkaline with 30% sodium hydroxide solution. The base, isolated by means of ether, was treated with excess of acetyl chloride in pyridine solution. The product crystallised from methyl alcohol in needles, m. p. 184° (Found: Cl, 14·6. $C_{14}H_{12}ONCl$ requires Cl, 14·45%).

By the hydrolysis of the acetyl derivative with alcoholic hydrochloric acid *4′-chloro-3-aminodiphenyl* was obtained. It separated from methyl alcohol in large needles, m. p. 82° (Found: Cl, 17·4.

$C_{12}H_{10}NCl$ requires Cl, 17·45%), and on oxidation with chromic anhydride in glacial acetic acid solution yielded *p*-chlorobenzoic acid (m. p. 240°).

2′ : 4′-*Dichloro*-3-*nitrodiphenyl* was obtained when dry chlorine was led into a mixture of 5 g. of 3-nitrodiphenyl and 1 g. of ferric chloride, heated at 100°, until the gain in weight was 2 g. The product was extracted with methyl alcohol and crystallised repeatedly from this solvent or from dilute acetic acid. It separated in needles, m. p. 115° (yield, 2—3 g.) (Found: Cl, 26·35. $C_{12}H_7O_2NCl_2$ requires Cl, 26·5%).

On reduction of the dichloro-compound with alcoholic stannous chloride solution in the presence of a large amount of concentrated hydrochloric acid, extraction of the free base, and acetylation, 2′ : 4 : 4′-*trichloro*-3-*acetamidodiphenyl* was obtained. It separated from dilute methyl alcohol in needles, m. p. 170° (Found: C, 53·6; H, 3·15. $C_{14}H_{10}ONCl_3$ requires C, 53·4; H, 3·2%).

2′ : 4 : 4′-*Trichloro*-3-*aminodiphenyl* was obtained on hydrolysis of the acetyl derivative. It separated from dilute methyl alcohol in needles, m. p. 105° (Found: Cl, 38·9. $C_{12}H_8NCl_3$ requires Cl, 39·1%).

Oxidation of the base with chromic anhydride in glacial acetic acid solution yielded 2 : 4-dichlorobenzoic acid (m. p. 161°). The introduction of the chlorine atom into the molecule during the reduction of the nitro-compound would lead to a product substituted in the ring containing the amino-group (compare Blanksma, *Rec. trav. chim.*, 1906, **25**, 365; Scarborough and Waters, this vol., p. 89); thus to the nitro-compound may be assigned the structure 2′ : 4′-dichloro-3-nitrodiphenyl.

Trichloro-3-*nitrodiphenyl* was obtained together with mono- and di-chloro-derivatives when chlorine was passed into a mixture of 3-nitrodiphenyl and ferric chloride at 100° for some hours. The product was extracted with acetone and repeatedly crystallised from this solvent or from benzene. It separated in needles, m. p. 211°. The yield was less than 20% of the theoretical (Found: Cl, 35·2. $C_{12}H_6O_2NCl_3$ requires Cl, 35·2%).

Tetrachloro-3-*nitrodiphenyl* was obtained when the chlorination was carried out at 120°. The product was extracted with acetone and recrystallised from this solvent repeatedly. It separated from alcohol as a matted mass of fine needles, m. p. 175° (Found: Cl, 42·5. $C_{12}H_5O_2NCl_4$ requires Cl, 42·2%).

4′-*Bromo*-3-*nitrodiphenyl*.—5 G. of 3-nitrodiphenyl were ground into a paste with 0·5 g. of ferric chloride, and 7 g. of bromine added. After the mass had cooled, water was added and the whole heated on the water-bath for 30 minutes. The product separated from

alcohol in plates, m. p. 95° (yield, almost theoretical) (Found : Br, 28·85. $C_{12}H_8O_2NBr$ requires Br, 28·8%).

4′-Bromo-3-aminodiphenyl was obtained on the reduction of the nitro-compound with stannous chloride in alcoholic hydrochloric acid solution. It separated from dilute alcohol in needles, m. p. 105° (Found : Br, 31·95. $C_{12}H_{10}NBr$ requires Br, 32·2%).

On acetylation of the base in pyridine solution *4′-bromo-3-acetamidodiphenyl* was obtained. It separated from alcohol in needles, m. p. 193° (Found : Br, 27·55. $C_{14}H_{12}ONBr$ requires Br, 27·75%). The base on oxidation with chromic anhydride in glacial acetic acid solution yielded *p*-bromobenzoic acid (m. p. 252°).

2 : 4 : 4′ : 6-Tetrabromo-3-aminodiphenyl.—2 G. of the monobromo-base and 5 g. of fused sodium acetate were dissolved in 50 c.c. of acetic acid. Excess of a 10% solution of bromine in acetic acid was added and the mixture gently warmed. The product, which separated on pouring into water, crystallised from alcohol in needles, m. p. 104° (Found : Br, 66·2. $C_{12}H_7NBr_4$ requires Br, 66·0%). On oxidation, in glacial acetic acid solution, with chromic anhydride, bromine was liberated and *p*-bromobenzoic acid (m. p. 251°) was isolated. Three bromine atoms must therefore be in the same ring as the amino-group, and the structure assigned depends partly on the direct bromination of 3-aminodiphenyl (see p. 3007).

3 : 4′-Dinitrodiphenyl.—A solution of 15 g. of 3-nitrodiphenyl in 250 c.c. of nitric acid (*d* 1·5) was kept over-night. The product, which separated when the mixture was poured into water, was digested with 500 c.c. of boiling methyl alcohol, the suspension allowed to cool, and the solid separated. It crystallised from acetone in pale yellow needles which melted, alone or mixed with the product of deamination of 3 : 4′-dinitro-4-aminodiphenyl (compare Scarborough and Waters, this vol., p. 1139), at 189°. Yield, 11—12 g.

2′ : 3-Dinitrodiphenyl was obtained on evaporation of the methyl alcohol used for the digestion of the crude nitration product. It separated from dilute acetic acid in white plates, m. p. 120° (compare Cain, J., 1912, **101**, 2298). Yield, 5—6 g. (Found : N, 11·5. Calc. : N, 11·5%). The structure of the compound was determined in the following manner : 2′ : 3-Dinitrobenzidine (Le Fèvre and Turner, J., 1926, 1759) was deaminated by grinding it to a paste with concentrated sulphuric acid, adding a little water and an excess of finely powdered sodium nitrite; followed by alcohol, and boiling the suspension under reflux for 30 minutes. The alcohol was partly removed and the dinitrodiphenyl separated. Crystallised from methyl alcohol and then from dilute acetic acid, it melted at 119°, alone or mixed with the product of direct nitration.

2′ : 3 : 4 : 4′-*Tetranitrodiphenyl* was prepared by dissolving 2·5 g. of either 2′ : 3- or 3 : 4′-dinitrodiphenyl in 60 c.c. of concentrated sulphuric acid and adding gradually 3 g. of finely ground potassium nitrate. The solution was kept over-night and then poured on crushed ice. The *tetranitro*-compound crystallised from methyl alcohol in pale yellow cubes, m. p. 173° (Found: C, 43·35; H, 1·8; N, 16·8. $C_{12}H_6O_8N_4$ requires C, 43·1; H, 1·8; N, 16·75%). When it was warmed with an excess of piperidine for 5 minutes, and the solution poured into dilute hydrochloric acid, 2′ : 3 : 4′-trinitro-4-piperidinodiphenyl separated; this crystallised from methyl alcohol in deep scarlet prisms, m. p. 143° (Found: C, 55·05; H, 4·4; N, 15·2. Calc.: C, 54·85; H, 4·3; N, 15·1%).

3-*Aminodiphenyl*.—A hot solution of 20 g. of 3-nitrodiphenyl in 200 c.c. of alcohol was added in portions to a solution of 120 g. of stannous chloride in 120 c.c. of hydrochloric acid, and the mixture refluxed for 4 hours. The tin double salt, which separated after removal of a part of the alcohol, was decomposed with 30% sodium hydroxide solution and the base was isolated by means of ether and distilled twice under diminished pressure (yield, 75%), b. p. 195°/15 mm., m. p. 30°.

3-Acetamidodiphenyl, prepared by refluxing a solution of the base in twice its weight of glacial acetic acid for 6 hours, separated from dilute alcohol in needles or small plates, m. p. 149°.

N-*Chloro*-3-*acetamidodiphenyl*.—10 G. of the acetyl derivative were suspended in a solution of 13 g. of sodium bicarbonate in 200 c.c. of water, and 150 c.c. of *N*-sodium hypochlorite added drop by drop with vigorous stirring. After 12 hours, the product was filtered off. It crystallised from light petroleum in masses of small needles, m. p. 87° (Found: available Cl, 14·1. $C_{14}H_{12}ONCl$ requires Cl, 14·4%).

4-*Chloro*-3-*acetamidodiphenyl*.—(a) *Conversion of the chloroamine*. The chloroamine was dissolved in alcohol and a few c.c. of acetic acid were added; the solution was refluxed for 30 minutes. The product separated from dilute alcohol in plates, m. p. 148°.

(b) *Direct chlorination of* 3-*acetamidodiphenyl*. Chlorine diluted with carbon dioxide was passed into a 2% solution of the acetyl derivative in acetic acid and in the presence of fused sodium acetate. After the theoretical gain in weight had been obtained, the solution was kept for some hours and then poured into water. The product, precipitated as a gum, after repeated crystallisations from methyl alcohol, separated in plates, m. p. 148° (Found: Cl, 14·5. $C_{14}H_{12}ONCl$ requires Cl, 14·4%).

On hydrolysis of the acetyl derivative with 10% alcoholic hydrochloric acid 4-*chloro*-3-*aminodiphenyl hydrochloride* was obtained.

It separated from dilute hydrochloric acid in needles, m. p. 247° (decomp.) (Found: HCl, 15·45; total Cl, 29·4. $C_{12}H_{10}NCl,HCl$ requires HCl, 15·2; Cl, 29·6%).

The decomposition of the salt with dilute aqueous ammonia gave a viscous oil which could not be obtained in a pure state. The salt was converted by the usual methods into 3 : 4-dichlorodiphenyl (m. p. 46°), and this compound on oxidation with chromic and acetic acids yielded 3 : 4-dichlorobenzoic acid (m. p. 198°).

4-*Bromo*-3-*acetamidodiphenyl*.—5 G. of 3-acetamidodiphenyl and 5 g. of fused sodium acetate were dissolved in 50 c.c. of acetic acid and treated with 45 c.c. of a 10% solution of bromine in acetic acid. After 1 hour, the mixture was poured into water; the precipitate obtained crystallised from dilute alcohol in plates, m. p. 163° (Found: Br, 27·4. $C_{14}H_{12}ONBr$ requires Br, 27·55%). On hydrolysis with 10% alcoholic hydrobromic acid, the base was obtained as a dark oil which decomposed on distillation under diminished pressure and separated as an oil from the usual solvents. The crude amine was converted, by the usual methods, into 3 : 4-*dibromodiphenyl*, a faintly yellow oil, b. p. 215°/15 mm. (Found: Br, 51·0. $C_{12}H_8Br_2$ requires Br, 51·2%). On oxidation with chromic and acetic acids 3 : 4-dibromobenzoic acid was isolated (m. p. 228°).

4 : 6-*Dibromo*-3-*acetamidodiphenyl*.—A solution of 5 g. of 3-acetamidodiphenyl and 15 g. of sodium acetate in 100 c.c. of acetic acid was refluxed and treated with 12 g. of bromine in portions. The product, which separated as a gum when the mixture was poured into water, crystallised from methyl alcohol in needles, m. p. 149°. The yield was some 50% of the theoretical, the residue being a gum (Found: Br, 43·55. $C_{14}H_{11}ONBr_2$ requires Br, 43·35%).

On hydrolysis of the acetyl derivative with alcoholic hydrobromic acid, the free base was obtained as a dark oil. This was converted into 2 : 4-*dibromodiphenyl*, a faintly yellow, viscid oil, b. p. 235°/15 mm. (Found: Br, 49·9. $C_{12}H_8Br_2$ requires Br, 51·2%). On oxidation with chromic and acetic acids 2 : 4-dibromobenzoic acid (m. p. 169°) was isolated. The symmetry of the molecule prevents a definite proof of the 4 : 6-structure; but from steric considerations it is more probable than the 2 : 4-structure.

4-*Bromo*-3-*aminodiphenyl Hydrobromide*.—5 G. of 3-aminodiphenyl were dissolved in carbon tetrachloride and treated with 50 c.c. of a 10% solution of bromine in the same solvent. The precipitated hydrobromide was filtered off and triturated with a fresh quantity of bromine solution. It separated from dilute hydrobromic acid in needles, m. p. 255° (decomp.) (Found: Total Br, 49·0.

$C_{12}H_{10}NBr,HBr$ requires Br, 48·65%). The structure was determined by liberating the base with dilute aqueous ammonia and subsequent acetylation, 4-bromo-3-acetamidodiphenyl (m. p. 163°) being obtained.

2 : 4 : 6-*Tribromo*-3-*aminodiphenyl*.—(a) 5 G. of 4-bromo-3-aminodiphenyl were dissolved in 100 c.c. of carbon tetrachloride and treated with 3·5 g. of bromine. The product was separated, suspended in fresh carbon tetrachloride, and treated with 3 g. of bromine. The solid product crystallised from alcohol, containing a little ammonia, in small needles, m. p. 141°. (b) 5 G. of 3-aminodiphenyl and 20 g. of fused sodium acetate were dissolved in acetic acid and treated with 180 c.c. of a 10% solution of bromine in acetic acid. After 1 hour the product was precipitated by pouring the mixture into water (Found : Br, 58·85. $C_{12}H_8NBr_3$ requires Br, 59·1%).

On oxidation of the base with chromic anhydride in glacial acetic acid solution, bromine was liberated and the molecule completely destroyed.

2 : 4 : 6-*Tribromodiphenyl* was obtained from the amine by the usual methods. It crystallised from methyl alcohol in needles, m. p. 64° (Found : Br, 61·7. $C_{12}H_7Br_3$ requires Br, 61·4%). Since oxidation with chromic anhydride caused complete decomposition, no definite proof can be given that the third bromine atom enters the 2-position; from a comparison with the behaviour of 2 : 4 : 4′ : 6-tetrabromo-3-aminodiphenyl, however, it may be reasonably assumed that all three bromine atoms are in one nucleus.

4-*Nitro*-3-*acetamidodiphenyl*.—A solution of 5 g. of 3-acetamidodiphenyl in a mixture of 30 c.c. of glacial acetic acid and 10 c.c. of acetic anhydride was heated to 70°, a solution of 1·5 c.c. of nitric acid (*d* 1·5) in 5 c.c. of acetic acid added drop by drop, and the temperature maintained for a further 30 minutes. The product, precipitated as a gum when the mixture was poured on ice, was extracted at once with alcohol, from which it separated in silky, pale yellow needles (yield, about 50%), m. p. 115° (Found : N, 11·1. $C_{14}H_{12}O_3N_2$ requires N, 10·95%).

On hydrolysis of the acetyl derivative with 10% alcoholic hydrochloric acid, 4-*nitro*-3-*aminodiphenyl* was obtained. It separated very slowly from dilute alcohol in orange needles, m. p. 116° (Found : N, 13·0. $C_{12}H_{10}O_2N_2$ requires N, 13·1%). The base on deamination yielded 4-nitrodiphenyl (m. p. 114°).

4′-*Nitro*-3-*acetamidodiphenyl*.—5 G. of 3-acetamidodiphenyl were dissolved in 100 c.c. of nitric acid (*d* 1·5) at 0°. After 15 minutes, the mixture was poured on ice, and the product, a gum, filtered off. After repeated crystallisations from alcohol, it separated in pale

yellow needles, m. p. 192° (yield, about 40%) (Found : N, 11·0. $C_{14}H_{12}O_2N_2$ requires N, 10·95%).

The acetyl derivative on hydrolysis yielded *4'-nitro-3-aminodiphenyl*, which separated from alcohol in long, orange needles, m. p. 137° (Found : N, 12·95. $C_{12}H_{10}O_2N_2$ requires N, 13·1%), and on oxidation with chromic and acetic acids yielded *p*-nitrobenzoic acid (m. p. 238°).

4-Bromo-4'-nitro-3-acetamidodiphenyl.—A solution of 5 g. of 4-bromo-3-acetamidodiphenyl in 100 c.c. of nitric acid (*d* 1·5) was kept for 20 minutes and then poured on ice. The product was immediately extracted with methyl alcohol, from which it separated slowly, on dilution, in yellow needles, m. p. 158° (yield, about 40%) (Found : N, 8·4. $C_{14}H_{11}O_3N_2Br$ requires N, 8·35%).

By the hydrolysis of this acetyl derivative with 10% alcoholic hydrochloric acid, *4-bromo-4'-nitro-3-aminodiphenyl* was obtained. It separated from dilute methyl alcohol in red needles, m. p. 145° (Found : N, 9·7. $C_{12}H_9O_2N_2Br$ requires N, 9·55%). The base on oxidation with chromic anhydride yielded *p*-nitrobenzoic acid (m. p. 238°).

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THE UNIVERSITY CHEMICAL LABORATORIES,
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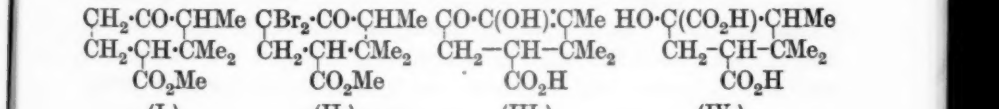
CCCCI.—*Derivatives of Methyl* 2 : 2-*Dimethylcyclopentan*-3-*one*-1-*carboxylate.*

By CHARLES STANLEY GIBSON, KELVOI VENKATAKRISHNA HARIHARAN, and JOHN LIONEL SIMONSEN.

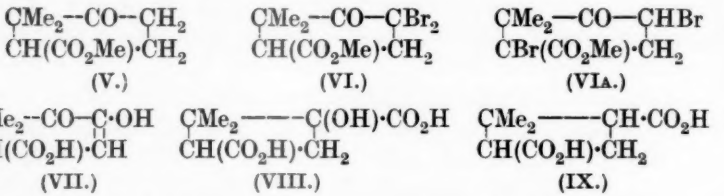
IT was shown recently that when methyl 2 : 2 : 3-trimethyl*cyclo*hexan-4-one-1-carboxylate (I) (J., 1925, **127**, 1294; this vol., p. 77) was brominated it yielded the dibromo-ester (II) and that this ester on treatment with alkali gave together with other products the hydroxyketo-acid (III) and the dibasic hydroxy-acid (IV).



(I.) (II.) (III.) (IV.)

It has appeared to us of interest to investigate whether *methyl* 2 : 2-*dimethylcyclopentan*-3-*one*-1-*carboxylate* (V) would on treatment with bromine and alkali behave in a similar manner, yielding the

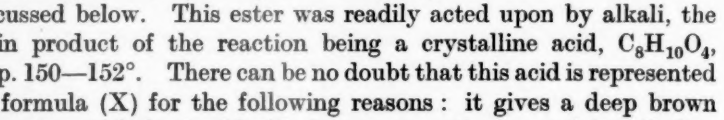
dibromo-ester (VI), the hydroxyketo-acid (VII) and a dibasic hydroxy-acid (VIII). The latter acid would be of particular importance, being the hydroxy-acid related to norpinic acid (IX), the synthesis of which has still to be effected.



(V.) (VI.) (VIA.)

(VII.) (VIII.) (IX.)

2 : 2-Dimethyl*cyclo*pentan-3-one-1-carboxylic acid was prepared by Perkin and Thorpe (J., 1904, **85**, 138), and by a modification of their process we have devised a method for obtaining it in excellent yield. When the *methyl* ester was brominated in acetic acid solution a crystalline *dibromo-ester* was obtained which is probably best represented by formula (VI); it is, however, not impossible that, in accordance with Wallach's views (*Annalen*, 1918, **414**, 296), the correct representation is by formula (VIA), and this will be further discussed below. This ester was readily acted upon by alkali, the main product of the reaction being a crystalline acid, $C_8H_{10}O_4$, m. p. 150—152°. There can be no doubt that this acid is represented by formula (X) for the following reasons: it gives a deep brown coloration with ferric chloride in aqueous solution and its alkaline solution is immediately oxidised by potassium permanganate; further, when oxidised with dilute nitric acid, it yields a mixture of dimethylmalonic acid and oxalic acid.



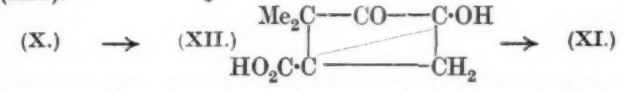
(X) (XI.)

4-*Hydroxy*-2 : 2-*dimethyl*-Δ^5-cyclo*penten*-3-*one*-1-*carboxylic acid* can, however, also react in its tautomeric form as the diketo-acid (XI), since on treatment with semicarbazide acetate it yields a *disemicarbazone* and with *o*-phenylenediamine a *quinoxaline* derivative. The ketohydroxy-acid showed no tendency to yield a lactone, giving with acetyl chloride a liquid acetyl derivative, and when it was distilled under diminished pressure, apart from the formation of an oil which was probably 3 : 3-*dimethyl*cyclo*pentane*-1 : 2-*dione*, the greater part of the acid was recovered unchanged. On titration, the acid behaved like a dibasic acid, the hydroxy-group being evidently activated by the adjacent carbonyl group.

Since the conversion of (XI) into (X) must proceed through the intermediate stage of (VII)—an example of $\alpha\beta$: $\beta\gamma$-tautomerism—an attempt was made to find the acid (VII) amongst the products

of the action of alkali on the dibromo-ester. An oil was separated which, unlike the Δ^5-acid, gave with ferric chloride a red coloration. This acid, which could not be obtained crystalline, gave on boiling with alkali a quantity of the crystalline Δ^5-acid, and on treatment with semicarbazide acetate and with *o*-phenylenediamine the disemicarbazone and the quinoxaline derivative of the diketo-acid were obtained. There seemed to be little doubt, therefore, that this liquid acid consisted essentially of 4-*hydroxy*-2 : 2-*dimethyl*-Δ^4-cyclo*penten*-3-*one*-1-*carboxylic acid*, and this view was confirmed by the formation of *as*-dimethylsuccinic acid on oxidation with dilute nitric acid.

The possibility that the constitution of the dibromo-ester should be represented by formula (VIA) remains to be investigated by studying the mechanism of the conversion of the Δ^5-acid (X) into the diketo-acid (XI), which may proceed by intramolecular tautomerism through the intermediate stage of the dicyclic ketohydroxy-acid (XII).



A large number of experiments were carried out with the object of converting both the Δ^4- and the Δ^5-acid into the dibasic hydroxy-acid (VIII), but no evidence of its formation has been obtained. Whether this is due to an actual inability of the *cyclo*pentane ring to pass into a *cyclo*butane ring or to the particular substituted ring used will form the subject of future experiments, which will also include the stereochemical investigation of the Δ^5-acid itself.

EXPERIMENTAL.

Ethyl $\beta\gamma$-*Dicyano*-β-*methylpentane*-$\gamma\varepsilon$-*dicarboxylate*.—To a solution of sodium (2·3 g.) in alcohol (30 g.), ethyl $\alpha\beta$-dicyano-β-methylbutyrate (18 g.) was added, the solution cooled, and ethyl β-iodopropionate (23 g.) gradually added, care being taken to avoid a rise of temperature (which produces a considerable quantity of ethyl acrylate). After remaining for 1 hour, during which time the temperature rose to about 40°, the reaction mixture was heated on the water-bath for 2 hours, water was then added, and the condensation product was isolated by extraction with ether and purified by distillation under diminished pressure. The whole distilled between 170° and 190°/5 mm. and on redistillation a large fraction was obtained, b. p. 184°/5 mm. (yield, 22 g.). *Ethyl* $\beta\gamma$-*dicyano*-β-*methylpentane*-$\gamma\varepsilon$-*dicarboxylate* is a faintly yellow, viscid oil with a somewhat unpleasant smell (Found: N, 9·8. $C_{14}H_{20}O_4N_2$ requires N, 10·0%).

β-*Methylpentane*-$\beta\gamma\varepsilon$-*tricarboxylic Acid*.—The dicyano-ester was

mixed with an equal volume of concentrated sulphuric acid, excessive rise of temperature being avoided, and when the mixture had cooled water was added until the solution was turbid. The hydrolysis was completed by boiling until evolution of carbon dioxide ceased and all the alcohol had evaporated, water being added from time to time to prevent charring (15 hrs.). From the cooled solution saturated with ammonium sulphate, the tricarboxylic acid was isolated by repeated extraction with ether. After crystallisation from hydrochloric acid it decomposed at 153—155°, but, as has been mentioned previously (*loc. cit.*, p. 1302), the m. p. is dependent on the rate of heating (Found: C, 49·8; H, 6·5. Calc.: C, 49·5; H, 6·4%).

The triethyl ester was obtained in a poor yield on esterification with alcohol and sulphuric acid; b. p. 161°/4 mm. (Found: C, 59·6; H, 8·6. Calc.: C, 59·6; H, 8·6%).

Ethyl 3 : 3-*Dimethyl*cyclo*pentan*-2-*one*-1 : 4-*dicarboxylate*.—Ethyl β-methylpentane-βγε-tricarboxylate (37 g.) was added to a suspension of finely divided sodium (5·6 g.) in benzene (100 c.c.), and the mixture warmed on the water-bath. A vigorous reaction took place and proceeded nearly to completion after removal of the source of heat; the last traces of sodium were dissolved by boiling for 1 hour. The deep brown solution was mixed with ice and made faintly acid with dilute sulphuric acid, and the benzene was separated, washed with sodium carbonate solution,* dried, and evaporated. The residual oil was distilled under diminished pressure; *ethyl* 3 : 3-*dimethyl*cyclo*pentan*-2-*one*-1 : 4-*dicarboxylate* was then obtained as a colourless oil, b. p. 145°/4 mm. (yield, 70%) (Found: C, 60·5; H, 8·1. $C_{13}H_{20}O_5$ requires C, 60·9; H, 7·8%). An alcoholic solution of the ester gave with ferric chloride a violet coloration.

2 : 2-*Dimethyl*cyclo*pentan*-3-*one*-1-*carboxylic Acid*.—The keto-ester was boiled with sulphuric acid (100 c.c.; 5%) under reflux for 6 hours. After addition of sodium carbonate sufficient to render the solution alkaline, the alcohol was removed on the water-bath and the solution was acidified and extracted with ether. On removal of the solvent the keto-acid crystallised immediately and had m. p. 108—109° as stated by Perkin and Thorpe (*loc. cit.*).

The *methyl* ester (V), prepared in the usual manner, had b. p. 158°/100 mm. (Found: C, 63·7; H, 7·9. $C_9H_{14}O_3$ requires C, 63·5; H, 8·2%).

Bromination of Methyl 2 : 2-*Dimethyl*cyclo*pentan*-3-*one*-1-*carboxylate*. *Methyl* 4 : 4-*Dibromo*-2 : 2-*dimethyl*cyclo*pentan*-3-*one*-1-*carboxylate* (VI).—A solution of the ester (17 g.) in acetic

* The sodium carbonate solution on acidification yielded a small quantity of a viscid oil which was not examined.

acid (17 c.c.) was kept at 5—10° while bromine (32 g.) in acetic acid (10 c.c.) was gradually added. The bromine was very rapidly absorbed with evolution of hydrogen bromide. When the addition was complete the mixture was poured on ice. A heavy oil was deposited which solidified. The *bromo*-ester crystallised from dilute methyl alcohol or dilute formic acid in long prisms, m. p. 76—77° (yield, 86%) (Found: Br, 48·8. $C_9H_{12}O_3Br_2$ requires Br, 48·8%).

Action of Barium Hydroxide on Methyl 4 : 4-*Dibromo*-2 : 2-*dimethyl*cyclo*pentan*-3-*one*-1-*carboxylate*.—To the bromo-ester (34 g.) a hot solution of barium hydroxide (96 g.) in water (250 c.c.) was added, and the reaction mixture boiled under reflux. A vigorous action ensued and in order to avoid loss of material it was necessary to remove the source of heat. The hydrolysis was completed by boiling for 45 minutes, and the pale yellow solution was then evaporated on the water-bath until free from alcohol, acidified, and repeatedly extracted with ether. On removal of the solvent a crystalline cake remained (17 g.). This was mixed with benzene (50 c.c.) and after digestion allowed to remain over-night in the ice-chest; the acid which was insoluble in benzene was then collected and the filtrate (A) reserved for later investigation.

The acid (m. p. 148—150°) crystallised from hydrochloric acid in glistening prisms, m. p. 150—152° (slight decomp.) (Found: C, 56·0; H, 5·9. $C_8H_{10}O_4$ requires C, 56·4; H, 5·9%).

4-*Hydroxy*-2 : 2-*dimethyl*-Δ^5-cyclo*penten*-3-*one*-1-*carboxylic acid* (X) was readily soluble in water, acetone, ethyl acetate and formic acid, very sparingly soluble in benzene, toluene, and light petroleum, somewhat more soluble in chloroform. It gave a brown coloration with ferric chloride and immediately decolorised alkaline potassium permanganate. In chloroform it rapidly absorbed bromine, but the bromo-acid decomposed with evolution of hydrogen bromide. From its deep yellow solution in concentrated sulphuric acid the acid could be recovered unchanged. On titration with alkali and phenolphthalein it behaved as a dibasic acid, but the end-point was not quite sharp (Found: *M*, 176. Calc.: *M*, 170). The acid decomposed when heated above its melting point, but it distilled under diminished pressure largely unchanged and showed no tendency to lactone formation. A small quantity of a neutral yellow oil was separated (b. p. 80—100°/4 mm.) which gave a deep red colour with ferric chloride and showed weakly acidic properties. The oil, which was readily soluble in water, yielded a resinous semicarbazone and a liquid phenylhydrazone. With *o*-phenylenediamine it gave an oil which appeared to be a quinoxaline derivative and it also gave a sparingly soluble, oily benzoyl deriv-

ative. Although, therefore, it was not possible to characterise the oil, there can be little doubt that it consisted of 3 : 3-*dimethyl*cyclo*pentane*-1 : 2-*dione* or its tautomerides.

When the ketohydroxy-acid (X) was digested with acetyl chloride it yielded an oil which was sparingly soluble in water but readily soluble in sodium bicarbonate solution. The oil was precipitated unchanged from the alkaline solution on acidification and doubtless consisted of 4-*acetoxy*-2 : 2-*dimethyl*-Δ^5-cyclo*penten*-3-*one*-1-*carboxylic acid*. On treatment with semicarbazide acetate it underwent hydrolysis, yielding the disemicarbazone described below.

The ketohydroxy-acid was recovered unchanged after prolonged digestion with potassium hydroxide solution (10%); on treatment with more concentrated alkali solutions or on fusion with potassium hydroxide at 200° some resinification took place with formation of deep red solutions, but the bulk of the acid was recovered unchanged.

The *disemicarbazone* of 2 : 2-*dimethyl*cyclo*pentane*-3 : 4-*dione*-1-*carboxylic acid* (XI) crystallised from dilute alcohol in needles, decomp. 200—201° (Found : C, 42·1; H, 5·5; N, 29·1. $C_{10}H_{16}O_4N_6$ requires C, 42·3; H, 5·6; N, 29·6%).

The *quinoxaline* derivative was prepared by boiling an alcoholic solution of the acid with an excess of *o*-phenylenediamine. It separated from benzene in pale yellow, irregular plates, m. p. 175—177° (Found : C, 69·2; H, 6·0. $C_{14}H_{14}O_2N_2$ requires C, 69·4; H, 5·8%).

Oxidation of 4-*Hydroxy*-2 : 2-*dimethyl*-Δ^5-cyclo*penten*-3-*one*-1-*carboxylic Acid with Nitric Acid*.—The ketohydroxy-acid (2 g.) was heated with nitric acid (*d* 1·2; 20 c.c.) on the water-bath for 12 hours, nitric acid (*d* 1·4; 5 c.c.) was added, and the mixture heated for a further 3 hours. After removal of the excess of mineral acid on the water-bath, during which process a small quantity of a volatile organic acid was evaporated with the steam, an oil remained which partly crystallised. An aqueous solution of the acid was treated with an excess of calcium chloride to remove oxalic acid and the filtrate was extracted with ether. On removal of the solvent, a solid cake remained which after crystallisation from hydrochloric acid decomposed at 187°. This acid was identified as dimethylmalonic acid by the method of mixed m. p. and by titration (Found : *M*, 133. Calc. : *M*, 132).

4-*Hydroxy*-2 : 2-*dimethyl*-Δ^4-cyclo*penten*-3-*one*-1-*carboxylic Acid* (VII).—The benzene solution (A) (see p. 3013) yielded on removal of the solvent a viscid brown oil which could not be induced to crystallise. It was readily soluble in water, gave a deep red coloration with ferric chloride, and immediately decolorised alkaline potassium permanganate. On treatment with semicarbazide acetate

and with *o*-phenylenediamine it yielded the derivatives of the diketo-acid described above. When it was boiled for some hours with a solution of potassium hydroxide (10%) partial conversion into the Δ^5-acid took place. It gave a liquid acetyl derivative and showed no tendency to lactone formation.

When the oil was oxidised with dilute nitric acid under the conditions used for the oxidation of the Δ^5-acid, *as*-dimethylsuccinic acid was obtained, m. p. 140—141°. This was identified by the method of mixed m. p. and by the preparation of the characteristic, sparingly soluble calcium salt.

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[*Received, November 3rd*, 1927.]

CCCCII.—*The Colouring Matters of Carajura.*

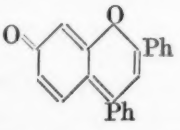
By ERNEST CHAPMAN, ARTHUR GEORGE PERKIN, and ROBERT ROBINSON.

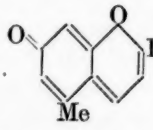
CARAJURA (Crajura, Chica red) (Crookes, "Handbook of Dyeing and Calico Printing," 1874, p. 388; Schützberger, "Traité des Matières Colorantes," 1867, p. 412) is a rare red pigment, prepared by the Indians of the Rio Meta and the Orinoco from *Bignonia Chica* for use as a flesh paint (compare Humboldt's "Travels," Edinburgh, 1836, p. 229). It is stated that the leaves, which on drying acquire a red colour, are extracted with water and that the extract is treated with a ground bark called *aryane*, which effects the precipitation of the colouring matter. This process is strongly suggestive of the enzymic hydrolysis of a glucoside. The yield is small and the preparation tedious, and for this reason the material appears to be of a costly character. Erdmann (Crookes, *op. cit.*) recognised the pigment nature of chica and stated that, after treatment with acid, it dyes mordanted cotton in shades similar to those derived from lac dye. He considered that the colouring matter was an isomeride of anisic acid and assigned to it the formula $C_8H_8O_3$.

The material employed in this investigation, obtained through the kindness of Messrs. Wright, Layman, and Umney, consisted of dull red fragments enclosed in crudely woven oblong bags, evidently of native production. It possessed a peculiar camphoraceous odour, was insoluble in water, alcohol, and dilute aqueous alkalis, and thus differed from that described by Crookes (*op. cit.*) as soluble in 36% alcohol and dilute aqueous alkalis. Examination of this sample of carajura showed that it was a very crude product con-

taining approximately 4% of colouring matter as calcium or magnesium lake, peaty organic matter, perhaps "aryane" (23%), in addition to a wax and a coloured resin in small relative amount. The mineral matter as ash (38%) consisted mainly of lime, magnesia, and silica together with some potassium carbonate. Some part of the calcium appears to be present as oxalate. A preliminary account of the isolation and properties of carajurin, the main crystallisable colouring matter of carajura, has already been published (Perkin, P., 1914, **30**, 212), but as the results of later work the empirical formula of carajurin is considered to be $C_{17}H_{14}O_5$ instead of $C_{18}H_{16}O_5$, as then suggested.

Carajurin, of which only 10 g. have been available for this investigation, crystallises from benzene in garnet-coloured, prismatic needles; it has phenolic properties and contains two methoxyl groups, so the formula may be expanded to $C_{15}H_7O_2(OH)(OMe)_2$. The most characteristic property of the substance is the ease with which it combines with acids, yielding well-defined, crystalline, orange-red oxonium salts from which the base may be easily recovered. For example, the sulphate, $C_{17}H_{14}O_5,H_2SO_4$, crystallises from dilute sulphuric acid in orange needles but is decomposed on boiling with water, and the hydrochloride loses hydrogen chloride at 100°. The analogy existing between carajurin and the hydroxybenzopyranol bases prepared by Bülow and his collaborators has already been commented upon ("The Natural Organic Colouring Matters," Perkin and Everest, 1918, p. 343) and is indeed striking; physically, carajurin closely resembles anhydro-7-hydroxy-2 : 4-diphenylbenzopyranol (1 : 4) (I) (Bülow and Sicherer, *Ber.*, 1901, **34**, 2380), which crystallises from benzene. A third crystalline member of the group has been recently obtained by Hirst (this vol., p. 2490) and this (II) exhibits a still closer resemblance to carajurin.

(I.) 

 (II.)

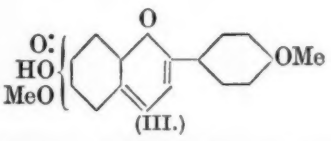
The composition of carajurin suggested that the connexion might be very close, because the colouring matter could be the anhydro-derivative of a dihydroxydimethoxyflavenol and thus be related to the large group of plant products that includes the flavones, flavonols, catechins, and anthocyanins. The coloured anhydrohydroxybenzopyranols have frequently been found to yield colourless derivatives of the hydroxybenzopyranols, and by the action of acetic anhydride and pyridine on carajurin a colourless *triacetyl* derivative, $C_{15}H_7O(OMe)_2(OAc)_3$, of hydrated carajurin was

obtained. Further confirmation of this view was found in the fact that fusion of carajurin with caustic alkali at 200° afforded *p*-hydroxybenzoic acid, whilst on boiling with concentrated aqueous potassium hydroxide, *p*-acetylanisole was obtained.

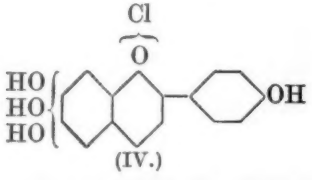
Bromination of carajurin in hot acetic acid solution gives, with remarkable ease, a compound, $C_{17}H_{12}O_5Br_4$ or $C_{17}H_{14}O_5Br_4$, which crystallises in orange needles and is apparently both a hydrobromide and a perbromide. On treatment with boiling acetone it is changed into *dibromocarajurin*, $C_{17}H_{12}O_5Br_2$, crystallising in bright red needles, bromoacetone being simultaneously produced.

Carajurin is completely demethylated on boiling with hydriodic acid and yields *carajuretin hydriodide*, $C_{15}H_{11}O_5I$, which has the composition and properties of a tetrahydroxyflavylium iodide. The action of cold pyridine on this salt leads to the formation of carajuretin, $C_{15}H_{10}O_5$, which occurs in scarlet needles and forms a colourless *penta-acetyl* derivative of hydrated carajuretin, $C_{15}H_7O(OAc)_5$.

On the supposition that the carajurin and carajuretin salts are flavylium derivatives it becomes of importance to note that these substances exhibit no tendency whatever to pass into pseudo-bases. Since the effect of a hydroxyl or methoxyl group in position 3 in the pyrylium nucleus in facilitating pseudo-base formation is well established, we concluded that carajurin is related to the flavone rather than to the flavonol group, that is, bearing in mind the formation of *p*-acetylanisole (above), that carajurin has the formula (III). Such a constitution, representing the substance as a



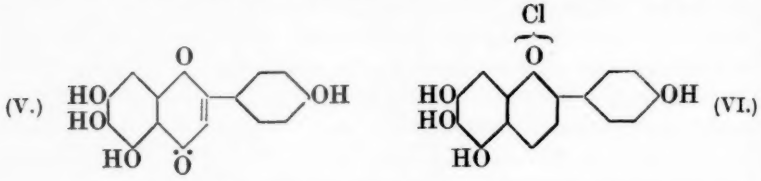
(III.)



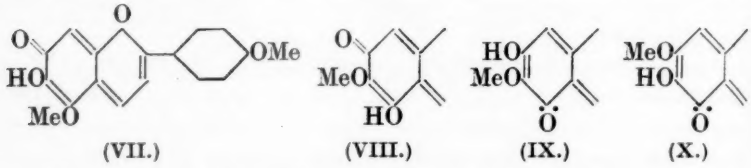
(IV.)

tetrahydroxybenzene derivative, served to explain the absence of phloroglucinol or other recognisable phenols from the alkali-fission products. Carajuretin hydrochloride, on this assumption, would conform to the type (IV), and in view of our strictly limited supply of the natural product we determined to synthesise flavylium salts of this nature in order to compare them with the carajuretin salts. The successful outcome of these synthetical investigations, which are described below, supplied the final proof of the correctness of the C_{17} formula for carajurin, and the fact that some of the salts which we prepared contain nuclear methyl groups is due to the uncertainty attached in the earlier stages to this question of the

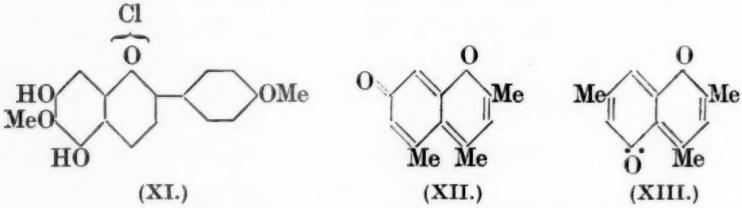
empirical formula. Guided by the assumed constitution of the flavone, scutellarein (V) (compare Bargellini, *Gazzetta*, **1915, 45**, i, 69; **1919, 49**, ii, 47), we prepared *scutellareinidin chloride* (VI) and



found that this salt was identical with carajuretin hydrochloride. This solved the major problem and left four possibilities for carajurin (VII, VIII, IX, X) differing only in the arrangement of substituents in the tetrahydroxybenzene nucleus; (VIII) and (IX) are tautomeric and would yield identical hydrochlorides (XI). This



5 : 7-dihydroxy-6 : 4′-dimethoxyflavylium chloride has been synthesised (see below) and it is not identical with carajurin hydrochloride. Moreover, the latter gives a ferric chloride colour reaction



indicating the existence of vicinal hydroxyl groups in the salt; (XI) exhibits no such reaction. The choice between (VII) and (X) cannot yet be made definitely, but (VII) is preferable on account of the colour and stability of carajurin. The analogies already quoted support the formula (VII), whereas (X) should be a violet or blue substance. In making this statement we are taking cognisance of unpublished observations on the anhydro-bases from 5-hydroxyflavylium salts, which are violet or blue and characterised by instability. The only recorded work bearing on this point is that of Collie and White (J., 1915, **107**, 369), who condensed orcinol with acetylacetone in presence of hydrogen chloride and isolated two structurally different hydroxytrimethylbenzopyrylium chlorides, of

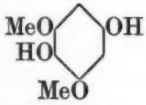
which one had a yellow and the other, obtained in smaller relative amount, an orange colour. The yellow salt gave a red quinonoid base (XII) and the orange salt gave a deep violet base (XIII). Provisionally, therefore, we suggest that carajurin has the formula (VII), and attempts to synthesise the colouring matter are in progress.

In addition to carajurin, carajura contains a second colouring matter, *carajurone*, $C_{15}H_9O_5 \cdot OMe$, which has been isolated in a micro-crystalline condition. This substance resembles carajurin in many of its properties, but is insoluble in benzene. It is probably a carajuretin monomethyl ether, but a clear proof of this is not available. Carajurin and carajurone dye mordanted fabrics in almost identical shades (see p. 3027), whereas those given by carajuretin are somewhat yellower. The red resin contained in carajura was not closely examined.

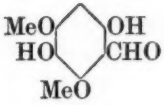
Derivatives of 1 : 2 : 3 : 5-*Tetrahydroxybenzene.*

The work involved in the synthesis of carajuretin necessitated the preparation of a number of partly methylated derivatives of 1 : 2 : 3 : 5-tetrahydroxybenzene and we have investigated more particularly those which may be used as the starting points of syntheses that can only proceed in one direction at each stage. We have had in mind not merely our immediate purpose but also the possibility of the synthesis, ultimately, of quercetagetin and gossypetin by such unambiguous methods.

The readily accessible 2 : 6-dimethoxyquinol (XIV) was the



(XIV.)



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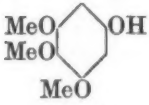

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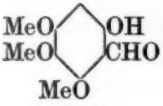


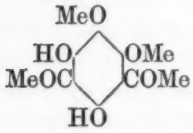
(XVII.)

starting point in many of our experiments; it could, for example, be directly condensed with anisoylacetone to a flavylium salt. On the other hand the introduction of the formyl group by Gattermann's method gave so poor a yield of the aldehyde (XV) that the process was useless for practical purposes. This was certainly due in part to the sparing solubility of dimethoxyquinol in ether, but also in all probability to its intrinsically small nuclear reactivity.

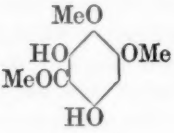
The methylation of dimethoxyquinol yields only antiarol (XVI) and tetramethoxybenzene, and we have confirmed the orientation of antiarol and worked out satisfactory conditions for its preparation. Antiarolaldehyde (XVII) could be obtained by an application of Gattermann's synthesis, but all attempts to prepare ketones such

as acetylantiarol and ω-methoxyacetylantiarol by the Hoesch method failed.

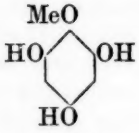
A series of experiments aiming at the *C*-acetylation of antiarol under varied conditions did not give the desired ketone, but two substances were isolated in small yield from the products of the action of aluminium chloride on antiarol and acetyl chloride in nitrobenzene solution. The first, m. p. 92—93°, gave analytical results agreeing with the formula (XVIII), whereas the second, m. p. 160—161°, is probably (XIX).



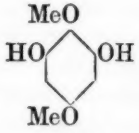
(XVIII.)



(XIX.)



(XX.)

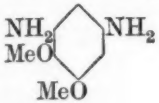


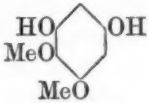
(XXI.)

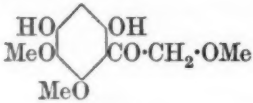
Bargellini and Bini (*Atti R. Accad. Lincei*, 1910, **19**, ii, 595; compare Bargellini, *Gazzetta*, 1919, **49**, ii, 47) isolated (*a*) tetramethoxyacetophenone, m. p. 48—50°, (*b*) a substance, m. p. 106—108°, regarded as 6-hydroxy-2 : 3 : 4-trimethoxyacetophenone, and (*c*) a substance, m. p. 162—163°, to which the formula (XIX) was assigned, from the products of interaction of 1 : 2 : 3 : 5-tetramethoxybenzene and acetyl chloride in carbon disulphide solution in presence of aluminium chloride. Repetition of the experiment gave (1) cream-coloured crystals, m. p. 177—178°, (2) yellow prisms, m. p. 111—112°, (3) brownish-yellow crystals, m. p. 162—163°, (4) 2 : 3 : 4 : 6-tetramethoxyacetophenone, m. p. 53—54°. The m. p. of a mixture of the substance, m. p. 160—161°, from antiarol with either (1) or (3) showed a large depression. It is hoped that further work will elucidate the nature of these substances and a detailed description is therefore postponed. It may also be pointed out that Nierenstein (J., 1917, **111**, 4) has ascribed the constitution (XIX) to a product, m. p. 166—168°, of the incomplete methylation of 2 : 3 : 4 : 6-tetrahydroxyacetophenone.

We have utilised iretol (XX) for the preparation of certain flavylium salts, although in this case the reactions could proceed in alternative directions. Investigation of the products showed that the hydroxyl in the *p*-position to the methoxyl group is the one which is involved in the ring closure. An interesting confirmation of this is found in the proof that the monomethyl ether of iretol, obtained by de Laire and Tiemann (*Ber.*, 1893, **26**, 2015) by treatment of the phenol with methyl-alcoholic hydrogen chloride, has the constitution (XXI). This and (XXIII) are the only possibilities and we have synthesised a dimethoxyresorcinol of the formula (XXIII) from 3 : 5-dinitroveratrole. A dilute aqueous solution of the hydro-

chloride of the corresponding diamine (XXII), containing a little stannous chloride, was boiled for many hours. The resulting phenol (XXIII) differs from de Laire and Tiemann's iretol monomethyl ether, a direct synthesis of which is being attempted.


(XXII.)

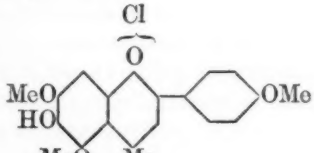

(XXIII.)

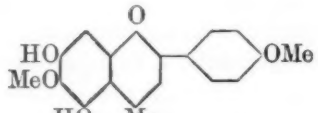

(XXIV.)

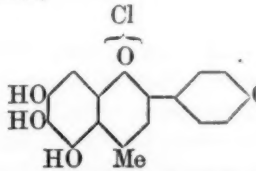
The dimethoxyresorcinols (XXIII and XXI) are the most suitable starting points in unambiguous syntheses of 3 : 5 : 6 : 7 : 3′ : 4′- and 3 : 5 : 7 : 8 : 3′ : 4′-hexahydroxyflavone, the constitutions, in all probability, of quercetagetin and gossypetin, respectively. In the former case we have demonstrated the feasibility of the scheme by the preparation of 2 : 4-dihydroxy-ω : 5 : 6-trimethoxyacetophenone (XXIV) from (XXIII) and methoxyacetonitrile in accordance with Hoesch's method (compare Slater and Stephen, J., 1920, **117**, 316). Test-tube experiments have convinced us that this ketone yields a flavonol derivative when it is heated with veratric anhydride and sodium veratrate (compare Allan and Robinson, J., 1924, **125**, 2192 and later communications).

Flavylium Salts derived from 1 : 2 : 3 : 5-*Tetrahydroxybenzene.*

Condensation of anisoylacetone and 2 : 6-dimethoxyquinol (XIV) in formic acid solution by means of hydrogen chloride gave (XXV), the alternative, a 4-anisyl-2-methylbenzopyrylium derivative, being excluded by the ready decomposition of the salt by alkalis with formation of *p*-acetylanisole and by analogy with the ascertained behaviour of benzoylacetone, for example, on condensation with phloroglucinol.


(XXV.)


(XXVI.)

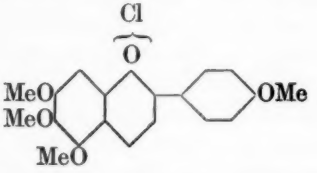

(XXVII.)

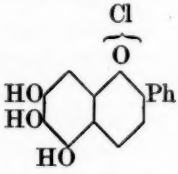
Anisoylacetone and iretol yield (XXVI) and on demethylation both

(XXV) and (XXVI) give 5 : 6 : 7 : 4′-*tetrahydroxy*-4-*methylflavylium chloride* (XXVII). Similarly 5 : 6 : 7 : 4′-*tetramethoxy*-4-*methylflavylium chloride* was obtained from antiarol and anisoylacetone.

The action of hydrogen chloride on a mixture of antiarolaldehyde (XVII) and *p*-acetylanisole in acetic acid solution led to the formation of 5 : 6 : 7 : 4′-*tetramethoxyflavylium chloride* (XXVIII); 5 : 7-dihydroxy-6 : 4′-dimethoxyflavylium chloride (XI) was obtained from iretol and anisoylacetaldehyde. On demethylation with hydriodic acid both salts (proof of structure of XI) gave *scutellareinidin iodide*; the *chloride* (VI) obtained from this was, as already stated, identified with carajuretin hydrochloride.

(XXVIII.)





(XXIX.)

Antiarolaldehyde, acetophenone, and hydrogen chloride yield 5 : 6 : 7-*trimethoxyflavylium chloride* and on demethylation the salt (XXIX) was obtained. This is the flavylium salt corresponding to the flavone baicalein (Shibata, Iwata, and Nakamura, *Acta Phytochim.*, 1923, **1**, 105; Bargellini, *Gazzetta*, 1919, **49**, ii, 47) and may be termed *baicaleinidin chloride*.

Experimental.

Carajurin.—Finely powdered carajura (100 g.) was extracted with boiling benzene to remove wax, which was found to interfere with the isolation of the colouring matters, and then digested with a mixture of water (600 c.c.) and concentrated hydrochloric acid (65 c.c.) at 95° for 15 minutes. After cooling, the dull red mass was collected, washed, and dried in the air and finally at 100° (A., 65 g.). Partial evaporation of the filtrate led to the separation of a red powder containing very little colouring matter and consisting chiefly of calcium oxalate; evaporation to dryness then gave a viscid residue containing organic matter and soluble salts of calcium, magnesium, and potassium, the former in preponderating amount.

The product A was extracted with boiling alcohol; the dull chocolate-coloured residue (ash, 26·5%) contained sand, and organic matter having a peaty nature. The orange-red alcoholic solution was evaporated to dryness on pure sand, and the powdered mass extracted with benzene for several hours in a Soxhlet apparatus (residue, B). The extract, after treatment with a little animal

charcoal, was filtered and concentrated; crystals were gradually deposited and the substance, after twice crystallising from benzene containing a trace of pyridine, was obtained in garnet-coloured needles, m. p. 205—207° (yield, 2·5 g.) (Found: C, 69·2, 68·6, 68·7, 68·1*, 68·1*; H, 4·7, 4·8, 4·9, 4·9*, 4·8* respectively; MeO, 19·8, 20·2, 20·6*, 20·4*, 20·5*. $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·1; 2MeO, 19·9%. $C_{17}H_{14}O_5$ requires C, 68·4; H, 4·7; 2MeO, 20·8%).

Carajurin is sparingly soluble in hot benzene and alcohol, but is more readily soluble in pyridine; it does not dissolve in boiling dilute aqueous ammonia (distinction from carajuretin) and dissolves sparingly in dilute aqueous caustic alkalis to orange-red solutions which become brown on keeping. The solubility of carajurin in cold dilute aqueous sodium hydroxide is best demonstrated by its immediate complete extraction by the alkali from a dilute benzene solution. Carajurin and alcoholic lead acetate give a solution which slowly deposits pale red needles, whereas alcoholic ferric chloride gives a brownish-violet solution which becomes brown on the addition of an excess of the reagent.

Carajurin hydrogen sulphate. A hot solution of carajurin in acetic acid containing sulphuric acid gave a gelatinous precipitate on cooling, but when a trace of water was added to the hot liquid, fine, orange-yellow needles separated; these were collected and washed with acetic acid (Found: C, 50·7; H, 4·4. $C_{17}H_{14}O_5,H_2SO_4$ requires C, 51·5; H, 4·1%). Further analyses gave conflicting results, but owing to the necessity for conserving our material the matter was not pursued. The salt is readily soluble in boiling water, but decomposition occurs and the solution soon deposits red crystals of carajurin, m. p. 204—206°.

The *hydrochloride* crystallises from acetic acid in glistening, orange leaflets and from 8% hydrochloric acid in woolly balls of orange filaments which, when quickly heated, darken at 120° and partly fuse at about 196°, becoming black. On prolonged heating at 100° or on boiling with water it yields carajurin. It is, however, stable in aqueous solution in the presence of a slight excess of hydrochloric acid.

Action of Bromine on Carajurin.—When a solution of bromine (0·4 g.) in acetic acid (2·1 c.c.) was added to one of carajurin (0·23 g.) in boiling acetic acid (18 c.c.), crystals at once separated (yield, 0·46 g.) (Found: Br, 50·8. $C_{17}H_{14}O_5Br_4$ requires Br, 51·7%). The glistening, orange-red leaflets darkened at 195° and had become a black powder at 300°; on boiling with water, hydrogen bromide passed into solution. This tetrabromide (0·3185 g.) dissolved when boiled with acetone (10 c.c.), but red needles quickly separated and

* Indicates micro-analysis throughout.

the odour of bromoacetone became apparent. The product (yield, 75·3% of the weight of tetrabromide; in another experiment, 74·1%) evidently consisted of a dibromocarajurin (Found: Br, 35·2. $C_{17}H_{12}O_5Br_2$ requires Br, 35·2%); it did not melt, but became a carbonaceous mass at 300°. It dissolved in dilute alkalis to red solutions that became brown on keeping. Theoretically a carajurin tetrabromide (or a dibromocarajurin dibromide, $C_{17}H_{12}O_5Br_4$) should give 74% of its weight of dibromocarajurin.

A curious result was obtained when the bromination was effected in commercial acetic acid solution, red needles, apparently consisting of a crude tribromocarajurin, being isolated (Found: Br, 46·4. Calc.: Br, 44·9%).

Fission of Carajurin with Alkalis.—By fusing carajurin with 10 parts of sodium hydroxide and a little water at 200°, dissolving the melt in water, acidifying the solution and extracting it with ether, a crystalline product was obtained containing *p*-hydroxybenzoic acid and a colourless, crystalline substance, m. p. 185—187°, which was sparingly soluble in water and gave no coloration with ferric chloride.

A dilute solution of carajurin in dilute aqueous-alcoholic potassium hydroxide was rapidly distilled. The red liquid became orange-yellow (opening of the heterocyclic ring) and at a later stage a dark oil separated. When the alkali became quite concentrated, a colourless oil distilled in the steam, and this was isolated by means of ether and identified as *p*-acetylanisole by conversion into the semicarbazone, m. p. 197°, alone or mixed with an authentic specimen.

O-*Triacetyldihydrocarajurinol.*—The red solution of carajurin (0·2 g.) and pyridine (0·6 c.c.) in acetic anhydride was kept for 3 days and then mixed with ice-cold dilute sulphuric acid. The pink precipitate was collected, washed, dried in the air, and dissolved in a very small volume of hot acetone. Crystals (0·07 g.) separated on keeping, and were obtained, on recrystallisation from methyl alcohol (charcoal), in colourless leaflets, m. p. 142° (Found*: C, 62·3; H, 5·1. $C_{23}H_{22}O_9$ requires C, 62·4; H, 5·0%). When this substance was boiled with a mixture of alcohol and concentrated hydrochloric acid, an orange-yellow solution of an oxonium salt was obtained; the addition of sodium acetate produced a red colour, and the pigment (probably carajurin) could be extracted by benzene, giving a red solution.

A second acetylated carajurin derivative, probably *O*-acetylcarajurin, was obtained by the prolonged action of cold acetic anhydride and a trace of sulphuric acid on the colouring matter; it crystallised in orange needles, m. p. 190—191°, but has not been closely examined.

Carajuretin.—After the methoxyl estimations (those carried out on the normal scale, not those in which Pregl's micro-method was used) the hydriodic acid was found to contain red needles of *carajuretin hydriodide*. These were collected, washed with sulphurous acid and then with water, and dried at 100° (Found: I, 31·6. $C_{15}H_{10}O_5$,HI requires I, 31·9%) (yield, 133·5% on the weight of carajurin employed. Calc., 134·1%). When hydriodic acid was added to a solution of this salt in hot alcohol, characteristic, fan-shaped clusters of fine, red needles separated.

The hydriodide dissolved at once in a small volume of cold pyridine and crystals soon separated from the solution; after the addition of boiling water and cooling, the scarlet needles were collected (yield, 68% on the weight of carajuretin hydriodide. Calc., 67·8%). The substance was recrystallised by concentrating a solution in much boiling alcohol and then adding boiling water, and *carajuretin* was thus obtained as a woolly mass of red needles that became black at 330° without exhibiting a melting point (Found: C, 66·7; H, 4·1. $C_{15}H_{10}O_5$ requires C, 66·7; H, 3·7%).

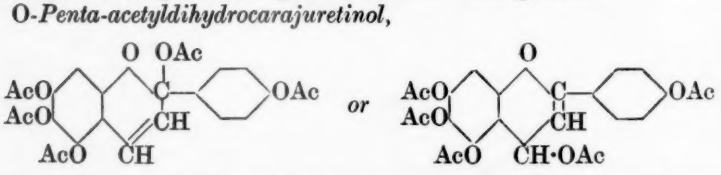
Carajuretin gives a fine crimson solution, becoming brown in the air, in aqueous ammonia or aqueous sodium carbonate. It gives a violet coloration with alcoholic ferric chloride, a dull reddish-violet precipitate with alcoholic lead acetate, and a deposit, probably of a monopotassium salt, with alcoholic potassium acetate. The substance combines with sulphuric acid in acetic acid solution to give the *hydrogen sulphate*, orange-yellow needles that can be crystallised from dilute sulphuric acid but are decomposed, with liberation of sulphuric acid (and probably carajuretin), on boiling with water.

The *hydrochloride* has been carefully examined for the sake of the comparison with the synthetical scutellareinidin chloride. Carajuretin hydriodide (0·9 g.) in hot alcoholic solution (100 c.c.) was decomposed by means of precipitated silver chloride. The filtered solution, mixed with a little hydrochloric acid, was concentrated; it then deposited prisms (0·53 g.) having an intense steel-blue lustre (Found* in material dried at 100°: C, 55·3, 55·5; H, 4·3, 4·2; Cl, 11·3, 11·0. $C_{15}H_{10}O_5$,HCl,H_2O requires C, 55·5; H, 4·0; Cl, 10·9%). The pure salt is sparingly soluble in alcohol to a brownish-orange solution; slightly impure specimens are readily soluble. Addition of a trace of ferric chloride to the alcoholic solution produces an intense brownish-violet coloration, which becomes reddish-brown on the addition of water. Addition of sodium carbonate to the alcoholic solution gives a fine permanganate-coloured liquid that becomes bluer on dilution with alcohol. The solution in aqueous sodium carbonate has a damson colour. The salt is sparingly soluble in cold 0·5% hydrochloric acid, but dissolves in the hot solvent;

on the addition of an equal volume of cold concentrated hydrochloric acid lustreless, woolly, orange needles are deposited, but if the liquid is heated, causing redissolution, and cooled very slowly, the substance separates completely in characteristic, elongated, rhombic prisms with a steel-blue lustre. These crystals are reddish-orange when viewed by transmitted light under the microscope and give a red smear on paper. Similarly the evaporation of an alcoholic solution of the chloride containing some 10% aqueous hydrochloric acid gives woolly needles that change in contact with the solvent into glistening, rhombic prisms. The salt is sparingly soluble in cold 7% sulphuric acid, but dissolves on heating: a gelatinous precipitate separates as the solution cools; on keeping, especially if warm, the amorphous material is replaced by very slender, orange-red needles. If aqueous perchloric acid (*d* 1·2) is added to the hot solution in 7% sulphuric acid, the *hydrogen perchlorate* quickly separates in clusters of short, orange-red needles exhibiting a bright metallic reflex.

The addition of bromine to a hot solution of carajuretin in acetic acid causes the immediate precipitation of minute, orange-red needles; these give hydrogen bromide to boiling water.

O-*Penta-acetyldihydrocarajuretinol*,



—A mixture of carajuretin (0·2 g.), pyridine (0·7 c.c.), and acetic anhydride (0·8 c.c.) was kept for 5 days; the red liquid was then added to ice-cold, dilute sulphuric acid and the pink precipitate was collected, washed, and dried on tile. An acetone solution of this product, after treatment with charcoal, was filtered and evaporated to dryness; the residue was dissolved in the minimum volume of boiling alcohol, and the solution allowed to cool. The cloudiness which then appeared was cleared by the addition of acetone drop by drop as required, and after 2 days the crystals (0·07 g.) were collected and twice recrystallised from benzene (charcoal). The colourless, prismatic needles, m. p. 156—157°, thus obtained were sparingly soluble in cold benzene and readily soluble in acetone (Found*: C, 60·3; H, 4·5. $C_{25}H_{22}O_{11}$ requires C, 60·2; H, 4·4%). This derivative discoloured on keeping in a specimen tube; it was reconverted into carajuretin hydrochloride by hydrolysis with alcoholic-aqueous hydrochloric acid and the characteristic lustrous, rhombic prisms of the salt were obtained. An acetyl estimation was carried out by Freudenberg's micro-

analytical method (*Annalen*, 1923, **433**, 230; Freudenberg and Weber, *Z. angew. Chem.*, 1925, **38**, 280) [Found: Ac, 42·8. $C_{15}H_7O(OAc)_5$ requires Ac, 43·2%].

Carajurone.—The residue B (see p. 3022) in the Soxhlet tube after removal of carajurin was extracted with boiling acetone and, after treatment with charcoal and filtration, the solution was concentrated to a small volume. Dark, granular material separated and this was washed with a little benzene and crystallised from acetone. *Carajurone* was thus obtained as an indistinctly crystalline, scarlet mass, m. p. 183—186° (decomp.) (Found* in material dried at 105° in a high vacuum: C, 67·1; H, 4·3; MeO, 11·6. $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·2; 1MeO, 11·1%) (an earlier analysis gave MeO, 11·4%).

Carajurone dissolves in aqueous sodium carbonate to a brownish-red solution, the colour of which is neither so intense nor so persistent on dilution as that obtained from carajuretin under similar conditions. The ferric chloride reaction in alcoholic solution closely resembles that given by carajurin; alcoholic lead acetate gives a maroon-coloured precipitate. The substance combines with strong acids, forming oxonium salts the solutions of which are brownish-orange, and there can be little doubt that it is carajuretin monomethyl ether. Definite evidence respecting the position of the methoxyl group, on this hypothesis, was not obtained, but the perceptible odour of *p*-acetylanisole observed on boiling a solution in concentrated aqueous sodium hydroxide is an indication that the methoxyl is in position 4′. The vapour evolved on destructive distillation of carajurone has an odour resembling that of *p*-hydroxybenzaldehyde.

Dyeing Properties.—Owing to its sparing solubility in water, crystalline carajurin dyes mordanted wool and cotton with difficulty; to overcome this, an alcoholic solution was poured into much water and satisfactory dyeings were then secured. The following comparative results were obtained on mordanted wool:

	Chromium.	Aluminium.	Tin.	Iron.
Carajurin.	Deep maroon.	Dull brownish-red.	Bright scarlet.	Deep violet-maroon.
Carajurone.	Deep maroon.	Dull brownish-red.	Dull scarlet.	Deep violet-maroon.
Carajuretin.	Brown.	Dull brownish-orange.	Brownish-scarlet.	Brownish-maroon.

Pyrogallol Trimethyl Ether.—The following modification of Ullmann's method (*Annalen*, 1903, **327**, 116) for the methylation of pyrogallol gives an 86% yield of a colourless product that does not require the subsequent treatment with ether recommended by Ullmann.

Aqueous sodium hydroxide (150 c.c. containing 60 g. of sodium hydroxide) was gradually added from a tap-funnel during 3—4 hours to a mixture of pyrogallol (42 g.), methyl sulphate (189 g.), and alcohol (100 c.c.) agitated vigorously by means of a gas-tight stirrer and contained in a flask (reflux condenser) from which air was excluded by hydrogen. After the completion of the reaction the vessel was cooled in an ice-bath and the addition of water (150 c.c.) caused the separation of the ether in glistening, white prisms, m. p. 47°. The average yield in many experiments was 48 g.

Antiarol (XVI).—2 : 6-Dimethoxybenzoquinone (24 g.) was obtained by Graebe and Hess's method (*Annalen*, 1905, **340**, 237; compare Will, *Ber.*, 1888, **21**, 608) from nitric acid (*d* 1·2) in 95% alcohol and pyrogallol trimethyl ether (40 g.).

Dimethoxyquinol, m. p. 160° (literature, 158°), was obtained by reduction of the quinone in 87% yield. It is stated to be easily soluble in ether, but we found that 100 c.c. of dry ether dissolved only 0·4 g. of the phenol. It is readily soluble in acetone, the simple alcohols, and acetic acid in the cold, but it is very sparingly soluble in carbon disulphide, nitrobenzene, benzene, toluene, chloroform, *iso*amyl ether, and light petroleum in the cold. It is partly on this account that we experienced so much difficulty in the preparation of an aldehyde from this phenol.

Will (*loc. cit.*; compare Bargellini and Bini, *Gazzetta*, 1911, **41**, ii, 8) obtained a trimethoxyphenol as a by-product in the preparation of 1 : 2 : 3 : 5-tetramethoxybenzene by methylation of 2 : 6-dimethoxyquinol with methyl iodide and methyl-alcoholic potassium hydroxide. The constitution of this substance was apparently first determined by Schlör (*Diss.*, 1889; compare Graebe and Suter, *Annalen*, 1905, **340**, 224; Kiliani on antiarol from *antiaris toxicaria*, *Arch. Pharm.*, 1896, **234**, 444; Thoms and Siebelung, *Ber.*, 1911, **44**, 2124), and as it was a matter of considerable importance in the present investigation we confirmed the relations exhibited in the scheme, using the method of mixed melting points.

The following conditions were employed for the semi-methylation of 2 : 6-dimethoxyquinol, the object aimed at being the complete

conversion of the quinol into antiarol and tetramethoxybenzene, because both substances were required and the separation of antiarol from dimethoxyquinol was difficult. A solution of sodium hydroxide (20 g.) in water (140 c.c.) was added to 2 : 6-dimethoxyquinol (34 g.) in a flask from which air was excluded by hydrogen. Methyl sulphate (32 g.) was then added in one portion with vigorous shaking, which was continued for 10—15 minutes and at intervals for 1 hour. 11 G. of 1 : 2 : 3 : 5-tetramethoxybenzene were isolated, and the alkali-soluble fraction (20 g.) was crystallised from ten times its weight of water and thus obtained in flat, white needles, m. p. 146° (yield 16·5 g.), and free from unchanged dimethoxyquinol.

Sodium antiarolate crystallised in silky, snow-white needles when a solution of antiarol in moderately concentrated aqueous sodium hydroxide was cooled.

O-*Acetylantiarol* (3 : 4 : 5-*trimethoxyphenyl acetate*), obtained by the action of boiling acetic anhydride and sodium acetate on the phenol, crystallised from not too much alcohol in colourless, transparent, elongated prisms, m. p. 74° (Found: C, 58·5; H, 6·3; MeO*, 40·8, 40·8, 40·7. $C_{11}H_{14}O_5$ requires C, 58·4; H, 6·2; 3MeO, 41·2%). The micro-analytical estimations of methoxyl in this readily purified substance gave slightly low results, and as those of carajurin were carried out in the same apparatus we considered that a similar small error would affect those determinations also. The first indication that carajurin has the formula $C_{17}H_{14}O_5$ rather than $C_{18}H_{16}O_5$ was obtained in this way.

3 : 6-*Dihydroxy*-2 : 4-*dimethoxybenzaldehyde* (XV).—Dry hydrogen cyanide in a stream of carbon dioxide and, by another delivery tube, a stream of hydrogen chloride, were simultaneously introduced into a warm solution of 2 : 6-dimethoxyquinol (3·5 g.) in ethyl acetate (100 c.c.). The slow passage of hydrogen chloride was continued for 2 hours and the flask was then stoppered and kept in the ice-chest. Next day, water was added to the reddish-green, dichroic solution so as to dissolve the small, dark-green deposit and the red, aqueous solution was then separated from the colourless ethyl acetate layer and boiled for a few minutes with passage of sulphur dioxide. On cooling, clumps of fine needles separated and these crystallised from hot water, containing sulphur dioxide, in very pale brown, feathery needles, m. p. 135—136° (Found: MeO*, 30·7. $C_9H_{10}O_5$ requires 2MeO, 31·3%). This substance, the yield of which was extremely poor, gives a sparingly soluble semicarbazone, and a golden-yellow solution in aqueous sodium hydroxide. It develops a green coloration, brown with excess of the reagent, on the addition of ferric chloride to its alcoholic solution.

Antiarolaldehyde (XVII).—In this experiment the use of sufficient

ether to dissolve the antiarol was found inadvisable and the quantities were so adjusted that all the phenol passed into solution before the separation of aldimine hydrochloride commenced. Hydrogen cyanide (from 10 g. of potassium cyanide), carried over in a slow stream of carbon dioxide, was introduced into a solution and suspension of finely powdered antiarol (6 g.) in anhydrous ether (300 c.c.), and a moderately rapid stream of hydrogen chloride led into the mixture (reflux condenser), which was frequently shaken. After 3 hours, glistening, white crystals began to be deposited and after 2 hours more, the stream of gas was interrupted and the vessel stoppered and kept over-night. The ethereal solution was decanted and the aldimine hydrochloride decomposed by heating on the steam-bath with water (30 c.c.) for a few minutes. The aldehyde, which separated as an oil and crystallised on cooling (4·7 g.), was recrystallised by the addition of warm water to its solution in hot methyl alcohol (yield, 4·45 g.). It was obtained in elongated, flat, white prisms, m. p. 65° (Found: C, 56·8; H, 5·8. $C_{10}H_{12}O_5$ requires C, 56·6; H, 5·7%). *Antiarolaldehyde* is slightly soluble in boiling water to a colourless solution, which becomes turbid on cooling and then deposits beautiful, star-shaped aggregates of needles. It is readily soluble in ether, alcohol, benzene, chloroform, acetic acid, and acetone. In aqueous or alcoholic solution it develops an intense brownish-violet coloration on the addition of ferric chloride; its solution in aqueous sodium hydroxide has a greenish-yellow colour. The *semicarbazone*, prepared in the usual manner, crystallised from 80% alcohol in slender, colourless needles that became yellow at 210° and melted with effervescence at 245° (Found: N, 15·4. $C_{11}H_{15}O_5N_3$ requires N, 15·6%).

Iretol Monomethyl Ether (XXI).—Picric acid (50 g.) gave recrystallised picryl chloride (30 g.) according to Jackson and Gazzolo's method (*Amer. Chem. J.*, 1900, **23**, 384); the addition of benzene in the crystallisation from alcohol, recommended by these authors, was found to be unnecessary.

Jackson and Boos (*Amer. Chem. J.*, 1898, **20**, 444) showed that the scarlet compound obtained by the action of sodium methoxide on picryl chloride yields methyl picrate on decomposition with water, but the method does not appear to have been used for the preparation of the substance in quantity. The following conditions gave good results. Sodium (4 g.) was dissolved in methyl alcohol (120 c.c.), and the solution added with shaking to one of picryl chloride (20 g.) in methyl alcohol (40 c.c.). After a short time, 80—100 c.c. of the methyl alcohol were distilled away and hydrochloric acid was added to the residue until it became yellow (acid reaction). Precipitation of the ether was completed by water and after one

crystallisation of the product from 60 c.c. of methyl alcohol it had m. p. 67—68° (yield, 18 g.) (Buttle and Hewitt, J., 1909, **95**, 1759, assign the m. p. 68° to the pure ether).

The conversion of methyl picrate into iretol was carried out by Kohner's method (*Monatsh.*, 1899, **20**, 928), and de Laire and Tiemann's work (*loc. cit.*) on the monomethylation of iretol from irigenin was confirmed with the synthetical material.

4 : 5-*Dimethoxyresorcinol* (XXIII).—The nitration of 4-nitroguaiacol (Pollecoff and Robinson, J., 1918, **113**, 647) required very careful control and the following method was used. Nitric acid (100 c.c.; *d* 1·42), cooled in ice to 0—3°, was mechanically stirred, finely powdered 4-nitroguaiacol (10 g.) was added in one portion, and 50 c.c. of nitric acid (*d* 1·42) at 0° were used to wash the stirrer and the sides of the container. The temperature rose and when it reached 11—12°, usually in 2 or 3 minutes, a large volume of water was added, precipitating the dinitroguaiacol as a bulky, yellow, crystalline mass (yield, 10·5 g.; m. p. 121—122°; the pure substance has m. p. 123°).

The dinitroguaiacol (15 g.) gave 4 : 6-dinitroveratrole (13·5 g., m. p. 97—98°; the pure substance has m. p. 101—102°) when heated with potassium carbonate and methyl sulphate in nitrobenzene solution.

A mixture of 4 : 6-dinitroveratrole (15 g.), granulated tin (50 g.), concentrated hydrochloric acid (150 c.c.), and water (50 c.c.) was shaken, the reaction being started by gentle heating on the steam-bath, subsequently moderated by the addition of water (20—30 c.c.), and finally completed by short heating on the steam-bath. The filtered liquid was evaporated to dryness under diminished pressure, air having been displaced by carbon dioxide, and the residue was dissolved in water. After removal of tin as sulphide, the filtered solution was evaporated to dryness under the conditions previously employed, leaving a white, crystalline crust (15 g.). This gave the *m*-diamine reaction with nitrous acid and a purple coloration with ferric chloride in aqueous solution. A solution of this product (17 g.) and stannous chloride (3·5 g.) in air-free water (1000 c.c.) was refluxed for 48 hours in a stream of carbon dioxide. Tin was eliminated as sulphide from the filtered, yellowish solution and the liquid was then concentrated to about 150 c.c. under diminished pressure (of carbon dioxide) and extracted with ether. The combined extracts were dried with sodium sulphate and filtered and the solvent was removed, finally under diminished pressure, leaving a brown oil that solidified on rubbing and was found to be free from nitrogenous material. This was dissolved in a little water, and lead acetate added, giving a small, flocculent precipitate. Lead

was eliminated as sulphide from the filtered solution, which was then evaporated to dryness under diminished pressure (carbon dioxide). The residue was dissolved in warm benzene; on slowly cooling, an oil separated; the benzene was decanted from this, and glassy crystals were then deposited. After recrystallisation from benzene the hard, transparent prisms, approximately tetrahedral in shape but possessing many facets, were dried in the air and then had m. p. 76—77°. When stored in an evacuated desiccator over calcium chloride, the crystals became at first sticky, adhering together, and then in a few days dry and friable again. The anhydrous material had m. p. 115—116° (Found*: C, 56·5; H, 5·9; MeO, 36·2. $C_8H_{10}O_4$ requires C, 56·4; H, 5·9; 2MeO, 36·5%). The solvent of crystallisation was also retained when the phenol was crystallised from chloroform; it was water, because, in a second experiment, the crude product was more thoroughly dried before the crystallisation from benzene and the crystals (1·1 g.) then melted at 105—110° and at 113° after recrystallisation.

The behaviour of this *dimethoxyresorcinol* with ferric chloride distinguishes it sharply from iretol monomethyl ether, the colorations developed in aqueous solutions being reddish-brown and blue respectively. A pine shaving, immersed in an alcoholic hydrochloric acid solution of the phenol, becomes mauve in colour.

Attempted Nuclear Acetylation of Antiarol.—There was no satisfactory outcome of experiments in which antiarol was (1) heated with acetic acid and zinc chloride, (2) treated with sulphoacetic acid at room temperature (compare Schneider and collaborators, *Ber.*, 1921, **54**, 1484, 2298, 2302; 1922, **55**, 1892), (3) boiled with acetic anhydride containing a little concentrated sulphuric acid (compare Brand and Collischonn, *J. pr. Chem.*, 1921, **103**, 338), (4) treated with acetyl chloride alone or in presence of anhydrous ferric chloride with or without carbon disulphide as solvent, (5) treated in anhydrous ether with acetonitrile (or methoxyacetonitrile) and hydrogen chloride, with or without the addition of zinc chloride.

Antiarol could not be carboxylated by means of potassium hydrogen carbonate, even in glycerol solution at 180° (stream of carbon dioxide) (compare Brunner, *Annalen*, 1907, **351**, 359); the phenol was recovered unchanged.

The relatively small nuclear reactivity of antiarol is of theoretical interest, a comparison with the much more reactive phloroglucinol dimethyl ether illustrating the depressing effect of the methoxyl group in the *m*-position to the free nuclear positions. An analogous phenomenon is the feeble reactivity of pyrogallol, in comparison with resorcinol, in the Hoesch reaction.

Acetyl chloride (10 c.c.) and then aluminium chloride (16 g.)

were added to a solution of antiarol (10 g.) in nitrobenzene (160 c.c.) and the mixture was heated for a short time on the steam-bath. The following products were isolated: (A). This was precipitated on addition of a little water to an alcoholic solution of the mixture; it crystallised from aqueous alcohol in stout, white needles, m. p. 92—93° (Found: C, 56·7, 56·7; H, 5·5, 5·7; MeO*, 24·1, 24·0. $C_{12}H_{14}O_6$ requires C, 56·7; H, 5·6; 2MeO, 24·4%). This substance, 4 : 5-*dimethoxy*-2 : 6-*diacetylresorcinol* (XVIII), is sparingly soluble in water, readily soluble in ether, and develops a deep red coloration with alcoholic ferric chloride. It dissolves in aqueous sodium hydroxide to a yellow solution and is not decomposed when the liquid is boiled.

After the separation of (A) a second substance (B) was isolated by taking advantage of its relatively sparing solubility in ether. It was only obtained in small amount, and crystallised from benzene in yellow prisms, m. p. 160—161° (Found*: MeO, 28·7, 28·9. $C_{10}H_{12}O_5$ requires 2MeO, 29·3%). (C) was obtained in minute amount from the ethereal solution, after separation of (A) and (B), in pearly plates, m. p. 78—84°, but owing to paucity of material it was not further investigated.

ω : 5 : 6-*Trimethoxyresacetophenone* (XXIV).—A solution of 4 : 5-dimethoxyresorcinol (0·75 g.) and methoxyacetonitrile (0·4 g.) in dry ether (30 c.c.) was saturated with hydrogen chloride and kept over-night. A clear solution resulted, but on the addition of fresh dry ether, colourless crystals were precipitated and these were separated and washed with ether. When an aqueous solution of this ketimine hydrochloride was heated on the steam-bath for a few minutes, the normal ready hydrolysis did not occur and ether extracted only a minute amount of the ketone. After being kept for several weeks, however, the aqueous solution gradually deposited yellow crystals, m. p. 128—129°. The substance crystallised from water in long, glistening, very pale yellow needles, m. p. 129—130° (Found*: C, 54·7; H, 5·9; MeO, 38·3. $C_{11}H_{14}O_6$ requires C, 54·5; H, 5·8; 3MeO, 38·4%). The ketone is readily soluble in alcohol and in boiling water; its solution in 10% aqueous sodium hydroxide is yellow, and after prolonged boiling, the unchanged substance, m. p. 129—130°, is recovered an acidification. The addition of ferric chloride to an alcoholic solution produces a holly-green coloration which fades to brown; in aqueous solution, the coloration is brownish-black.

Anisoylacetone.—Besthorn and Jaegli (*Ber.*, 1894, **27**, 810) employed alcohol-free sodium ethoxide for the condensation of *p*-acetylanisole and ethyl acetate. We have used sodamide as the condensing agent. Finely powdered sodamide (4 g.) was

added to a mixture of *p*-acetylanisole (15 g.), ethyl acetate (22 g.), and dry ether (70 c.c.). A brisk reaction (reflux) supervened and the mixture was occasionally shaken during an hour and then warmed for a few minutes on the steam-bath. The sodium salt was separated and after acidification of its aqueous solution with acetic acid, a product, m. p. 55—56°, was isolated (8·1 g.). After crystallisation from methyl alcohol the m. p. was 57° (literature, 54·5°).

6-*Hydroxy*-5 : 7 : 4′-*trimethoxy*-4-*methylflavylium Chloride* (XXV). —A mixture of 2 : 6-dimethoxyquinol (3·4 g.), anisoylacetone (4 g.), and formic acid (50 c.c.; 98—100%) was saturated with hydrogen chloride for several hours and next day the oxonium salt was precipitated as a red, crystalline powder (5·5 g.) by the addition of ether. The *chloride* crystallised from dilute hydrochloric acid in stellar aggregates of slender, red needles (Found in material dried in a vacuum over potassium hydroxide: C, 58·4; H, 5·7. $C_{19}H_{19}O_5Cl,1{\cdot}5H_2O$ requires C, 58·5; H, 5·7%). On heating, the salt lost water at 120° and then melted with decomposition at 139° to 145° according to the rate of heating. It dissolves in hot water to a red solution and in hot dilute hydrochloric acid to an orange solution. Addition of sodium carbonate to an aqueous solution gives a deep red liquid tinged with purple; on keeping, it becomes turbid and yellow. The reaction with sodium hydroxide is similar, but the change is more rapid. Sodium acetate, added to an aqueous solution, gives the pseudo-base as a dirty grey precipitate. The intensely golden-yellow solution in sulphuric acid does not exhibit fluorescence. Ferric chloride gives no characteristic reaction. After a solution of the salt in 20% aqueous potassium hydroxide had been refluxed for 1 hour (atmosphere of hydrogen), *p*-acetylanisole was isolated from the products by means of ether. The semicarbazone crystallised from alcohol in needles, m. p. 197°, alone or mixed with an authentic specimen. The *ferrichloride* crystallised from acetic acid in flat, elongated prisms, m. p. 205°, that are reddish-brown by reflected light and pale orange-brown by transmitted light (Found: C, 43·7; H, 3·8. $C_{19}H_{19}O_5Cl_4Fe$ requires C, 43·4; H, 3·7%).

5 : 7-*Dihydroxy*-6 : 4′-*dimethoxy*-4-*methylflavylium Chloride* (XXVI).—A moderately rapid stream of hydrogen chloride was passed through a mixture of iretol (1·6 g.), anisoylacetone (2 g.), and formic acid (30 c.c.; *d* 1·2) for 2 hours. The glistening, red prisms that separated (3·25 g.) crystallised from 3% hydrochloric acid (1 g. required about 400 c.c.) in shining, red needles, which became duller on being kept in a vacuum over sodium hydroxide for 3 days (Found: C, 60·0; H, 5·2. $C_{18}H_{17}O_5Cl,0{\cdot}5H_2O$ requires

C, 60·4; H, 5·1%). This specimen darkened rapidly at 100—105°, was very dark at 120°, shrank at 135°, became black at 150°, and melted with vigorous decomposition at 208°. On the other hand, an air-dried specimen lost water at 120°, but the salt darkened very slowly; it blackened from 170° to 190° and melted with vigorous decomposition at 208°.

The chloride is moderately readily soluble in water and alcohol, giving bright red solutions, and is sparingly soluble in dilute hydrochloric acid, the solution being reddish-orange. The reddish-yellow solution in sulphuric acid becomes deep red on warming. Sodium carbonate, added to an aqueous solution, gives a purplish-red coloration, persistent even on boiling, but with sodium hydroxide the red colour changes to yellow and on boiling the odour of *p*-acetylanisole becomes apparent. This salt exhibits no characteristic ferric chloride reaction, a fact of interest in connexion with the constitution of carajurin.

Addition of sodium acetate to a solution of the chloride caused the separation of the red anhydro-base as an oil, which solidified and was soluble in hot benzene to a deep red solution.

The *ferrichloride* crystallised from acetic acid in compact, rhombic prisms, m. p. 180—181° with slight previous darkening (Found: C, 42·3; H, 3·5. $C_{18}H_{17}O_5Cl_4Fe$ requires C, 42·3; H, 3·4%). The crystals were red in mass, exhibited a blue metallic lustre, and appeared brown when viewed by transmitted light.

5 : 6 : 7 : 4′-*Tetramethoxy*-4-*methylflavylium Ferrichloride*.—A mixture of antiarol (2·7 g.), anisoylacetone (3 g.), and formic acid (35 c.c.; *d* 1·2) was treated with hydrogen chloride for 6 hours, and the saturated solution then kept for several days. The *chloride*, precipitated by ether (4·6 g.), crystallised from dilute hydrochloric acid in slender, silky, orange-red needles, m. p. 143—144° (decomp. and previous darkening). The *ferrichloride* crystallised from acetic acid in golden-yellow needles, m. p. 176° (Found: C, 44·5; H, 4·0. $C_{20}H_{21}O_5Cl_4Fe$ requires C, 44·5; H, 3·9%).

5 : 6 : 7 : 4′-*Tetrahydroxy*-4-*methylflavylium Chloride* (XXVII).—(A) *From the trimethyl ether* (XXV). In our earlier experiments we obtained a specimen of the demethylated chloride in the usual manner; it formed reddish-brown prisms exhibiting a bluish-green lustre (Found: C, 57·8; H, 4·7; Cl, 10·3; loss at 105—110° in a high vacuum, 2·7. $C_{16}H_{13}O_5Cl,0·5H_2O$ requires C, 58·3; H, 4·3; Cl, 10·8; H_2O, 2·7%. The monomethyl ether, $C_{17}H_{15}O_5Cl,H_2O$, requires C, 57·9; H, 4·9; Cl, 10·1; H_2O, 5·1%). It was clearly impossible to be sure that demethylation was complete and the process was therefore investigated quantitatively. A specimen of the initial material (XXV) was twice crystallised from 7%

hydrochloric acid and dried in a vacuum desiccator over sodium hydroxide; it differed somewhat from that described above and, on heating, lost water at 120° and melted at 142—143° with effervescence (Found: C, 49·9; H, 6·0%). We suspect that this product may have had the composition $C_{19}H_{19}O_5Cl,HCl,3H_2O$, which requires C, 50·3; H, 5·8%, but it was sufficient for our purpose that the analysis indicated that it contained 71·4% of the anhydro-base $C_{19}H_{18}O_5$. When the salt (0·3156 g.), mixed with phenol (8·0 g.) and hydriodic acid (20 c.c.; *d* 1·7), was heated at 135—145° in an atmosphere of carbon dioxide, demethylation was complete after 3 hours (Found: MeO, 19·8. Calc.: MeO, 20·4%), and this was confirmed in two further experiments. In the absence of phenol, however, demethylation was incomplete (Found: MeO, 17·7%). The *iodide* was isolated, after the addition of ether, in lustrous, brownish-red, diamond-shaped plates that appeared pale brown by transmitted light. Addition of hydriodic acid to its hot solution in alcohol caused the separation of characteristic, glistening, radiating clusters of flat, red needles. On heating, it began to shrink and darken at 278° and melted with decomposition at 290°. When treated with pyridine (compare the behaviour of the lower homologue carajuretin hydriodide, p. 3025), the salt dissolved, but on stirring, needle crystals, changing to prisms, separated. The anhydro-base could not be isolated in a sufficiently pure form for analysis.

The *chloride* was prepared from the iodide in alcoholic solution in the usual manner by means of silver chloride. It was twice recrystallised by the addition of concentrated hydrochloric acid to its alcoholic solution, which was then concentrated and cooled, and was obtained in reddish-brown, oblique, frequently twinned prisms. The smaller crystals appeared reddish-brown, but the larger ones had a bluish-green metallic reflex (Found in material dried in a vacuum over sodium hydroxide: C, 58·5; H, 4·5. $C_{16}H_{13}O_5Cl,0·5H_2O$ requires C, 58·3; H, 4·3%). A specimen was again crystallised (Found: C, 58·6; H, 4·4%). The salt gradually darkened above 200°, lost its lustre at about 255°, and became very dark at 270°, but did not melt at 320°. It is sparingly soluble in cold water and moderately readily soluble in hot water to a red solution. Other properties are mentioned below.

(B) *From the dimethyl ether* (XXVI). The chloride (0·3—0·4 g.) was demethylated by means of hydriodic acid (20 c.c.; *d* 1·7) in presence of phenol (8 g.) for 3 hours at 135—145° with passage of carbon dioxide. The methyl iodide was absorbed in pyridine (Found: MeO, 16·7, 16·6. Calc.: MeO, 17·3%). The isolated *iodide* had all the properties mentioned above under (A), but the

chloride, in this case very sparingly soluble in alcohol, crystallised in well-formed, hexagonal tablets, reddish-brown by transmitted light and exhibiting a splendid green lustre (Found : C, 59·9; H, 4·1. $C_{16}H_{13}O_5Cl$ requires C, 59·9; H, 4·1%). The crystals separated from a hot solution during the distillation of the alcohol and this may account for their anhydrous character, but the superficial difference between this specimen and the one obtained as above under (A) was sufficiently great to give us at first the impression that the substances were structurally different. Further experiments and comparison with the analogous case of scutellareinidin chloride have made it clear that the chlorides from (A) and (B) were, in fact, identical, although the latter was the purer specimen. The behaviour on heating was the same as that cited above (under A) and all the reactions and solubility relations of the two specimens were found to be identical. The salt is a homologue of carajuretin hydrochloride and in some of its properties resembles this substance. A solution in aqueous sodium carbonate has a brownish-cherry-red colour, but on dilution with alcohol the change of shade towards blue is not so pronounced as is the case with carajuretin. The damson solution in aqueous sodium hydroxide is not so intensely coloured as an equivalent solution of carajuretin and when it fades it becomes more brownish-yellow. The colour reaction with ferric chloride in alcoholic solution was brownish-red; the violet tinge observed with carajuretin was absent. For purposes of comparison of the specimens prepared as under (A) and (B), the behaviour of the salt with acetone, chloroform, sodium acetate, ammonia, concentrated hydrochloric and sulphuric acids was observed, but the details need not be recorded.

5 : 6 : 7 : 4′-*Tetramethoxyflavylium Chloride* (XXVIII).—A mixture of antiarolaldehyde (4·2 g.), *p*-acetylanisole (3 g.), and acetic acid (10 c.c.) was saturated with hydrogen chloride at 60° for 6 hours; on cooling and keeping, bright red needles were copiously deposited (6·5 g.). On heating, the salt lost water at 100—120°, darkened at 140°, and had m. p. 145—146° (decomp.). It is sparingly soluble in cold water, acetone, or dilute hydrochloric acid, more readily soluble in alcohol, and all its solutions have a golden-yellow colour. The amber-yellow solution in concentrated sulphuric acid did not fluoresce and on heating became bright red and then deep red. The *ferrichloride* crystallised from acetic acid in orange, elongated prisms, m. p. 170° (Found : C, 43·5; H, 3·8. $C_{19}H_{19}O_5Cl_4Fe$ requires C, 43·4; H, 3·7%).

5 : 6 : 7 : 4′-*Tetrahydroxyflavylium Chloride* (*Scutellareinidin Chloride, Carajuretin Hydrochloride*) (VI).—A mixture of tetramethoxyflavylium chloride (2·5 g.), phenol (8 g.), and hydriodic

acid (70 c.c.; *d* 1·7) was boiled in an atmosphere of carbon dioxide for 20—30 minutes. The salt passed into solution, but glistening, deep red crystals slowly separated again and, after cooling, these were isolated (2·2 g.). The substance decomposed from 200—270° without melting.

The iodide was converted in the usual manner into the *chloride*, which crystallised from alcohol, containing concentrated hydrochloric acid, in shining, reddish-brown plates exhibiting a green reflex (Found: C, 59·3, 59·5; H, 4·1, 4·1. $C_{16}H_{13}O_5Cl$ requires C, 59·9; H, 4·1%). As a result of later work we now regard this substance as consisting essentially of a *scutellareinidin chloride monomethyl ether*. It does not melt below 285°.

Demethylations were then effected in which the amount of methyl iodide produced was estimated. The 5 : 6 : 7 : 4′-tetramethoxyflavylium chloride employed was crystallised from 10% hydrochloric acid and obtained in hair-fine, red needles which were dried in a vacuum over sodium hydroxide. As before, the m. p. was 145—146° (decomp.), but the chlorine content (11·3%) indicated a complex constitution ($C_{19}H_{19}O_5Cl$ requires Cl, 9·8%). The theoretical methoxyl content was therefore calculated from the results of combustions (Found: C, 55·2, 55·4; H, 5·7, 5·8; and hence complete demethylation requires MeO, 30·1%). The salt (0·3038 g.) was heated at 135—145° with hydriodic acid (20 c.c.; *d* 1·7) for 2·5 hours (Found: MeO, 22·9. Calc.: for 3MeO, 22·6%); in later experiments the quantities of the salt and of hydriodic acid were similar. Addition of 2 g. of phenol raised the methoxyl eliminated to 24·6%; 6 g. raised it to 28·3%; and using 8 g. of phenol and heating for 3 hours, we found MeO, 29·5% in two experiments. The last conditions were accordingly employed in the preparation of scutellareinidin iodide, and the phenol and hydriodic acid were always heated together at 135—140° to remove impurities before the introduction of the flavylium salt. The *iodide* was collected after the addition of ether and had all the properties previously mentioned as characteristic of carajuretin hydriodide. The *chloride* crystallised from alcohol–concentrated hydrochloric acid in reddish-brown, rhombic tablets exhibiting a dark green metallic lustre (Found in material dried in a vacuum over sodium hydroxide: C, 58·6; H, 3·8. $C_{15}H_{11}O_5Cl$ requires C, 58·7; H, 3·6%). This specimen, therefore, was anhydrous, whereas carajuretin hydrochloride crystallised with $1H_2O$; nevertheless a direct comparison showed that the substances were identical, and this is a further example of the small reliance to be placed on the extent of hydration of flavylium salts as a guide to their individuality. Another case is mentioned above and it may be recalled that Malkin and

Robinson (J., 1925, **127**, 1190) obtained two specimens of pelargonidin chloride 3 : 4′-dimethyl ether, only one of which persistently crystallised in a hydrated form. All the reactions and properties given above under the heading "carajuretin hydrochloride" were also found to be characteristic of scutellareinidin chloride and a specimen of the latter having the steel-blue appearance of the former was obtained by repeated crystallisation. Finally, scutellareinidin chloride was converted into an acetyl derivative of the pseudo-base as previously described for the carajuretin derivative. The substance had m. p. 156—157°, alone or mixed with *O*-penta-acetyldihydrocarajuretinol, and the other properties of the specimens exhibited no divergences.

5 : 7-*Dihydroxy*-6 : 4′-*dimethoxyflavylium Chloride* (XI).—A solution of *p*-anisyl β-hydroxyvinyl ketone (from 4 g. of the copper derivative) in dry ether (100 c.c.) was added to one of iretol (2·2 g.) in dry ether (200 c.c.), and the mixture saturated with hydrogen chloride for 6 hours. The red solid was separated (4 g.) and extracted with very dilute hydrochloric acid; the filtered solutions deposited microscopic red crystals, which were recrystallised from 9% hydrochloric acid, only 0·18 g. of the pure salt being obtained. The salt was also obtained and in rather better yield by using dry ethyl acetate as the solvent; it crystallised in minute, red needles (Found*: MeO, 17·4. $C_{17}H_{15}O_5Cl,H_2O$ requires 2MeO, 17·6%). It did not melt at 260° and was moderately readily soluble in alcohol and in water to red solutions that gave no distinctive coloration with ferric chloride. A further distinction from carajurin hydrochloride was the solubility in aqueous sodium carbonate to a red solution.

The chloride (0·16 g.) was added to phenol (4 g.) and hydriodic acid (10 c.c.; *d* 1·7), and the mixture boiled with passage of carbon dioxide for 1·5 hours. After cooling and addition of ether, the demethylated iodide (0·13 g. of maroon needles) was collected and transformed into the chloride in the usual manner. This salt (yield, 0·08 g.) crystallised from alcohol–concentrated hydrochloric acid in clumps of dark reddish-brown, flat prisms or plates having a bluish-green reflex. On solution in 0·5% hydrochloric acid and addition of concentrated hydrochloric acid, woolly, orange-red needles were obtained and on reheating and slow cooling, glistening, rhombic prisms exhibiting a steel-blue reflex were deposited. The colour of the acid solutions, the solubility relations, and the reactions with alkalis and with ferric chloride were all identical with those of scutellareinidin chloride and carajuretin hydrochloride. The preparation of *O*-penta-acetyldihydrocarajuretinol could not be attempted in this case owing to paucity of material and the poor yield in the acetylation.

5 : 6 : 7-*Trimethoxyflavylium Salts.*—A mixture of antiarol-aldehyde (5·6 g.), acetophenone (3·2 g.), and acetic acid (10 c.c.) was saturated with hydrogen chloride at 65—70° for 6—7 hours. After keeping for 12 hours, the flavylium chloride was precipitated by the addition of ether as a reddish-brown, crystalline mass; this crystallised from 9% hydrochloric acid (100 c.c.) in slender, golden-yellow, silky needles (yield, 8·2 g.) which darkened at 110° and had m. p. 124—125° (decomp.). The salt is readily soluble in hot water, hot dilute hydrochloric acid, cold alcohol, or acetone to golden-yellow solutions. Its amber-yellow solution in sulphuric acid becomes bright red and then deep red on heating; consequently this reaction, shared with many other substances described in this communication, is due to the tetrahydroxybenzene nucleus. The cream-coloured pseudo-base is precipitated by the addition of sodium acetate or sodium carbonate to an aqueous solution of the chloride. The *ferrichloride* crystallises from acetic acid in well-formed, deep red prisms, m. p. 151°, exhibiting a bluish glance and appearing brownish-yellow by transmitted light (Found: C, 43·9; H, 3·5. $C_{18}H_{17}O_4Cl_4Fe$ requires C, 43·7; H, 3·5%). The derivative is readily soluble in acetone to a red solution.

5 : 6 : 7-*Trihydroxyflavylium Chloride* (*Baicaleinidin Chloride*) (XXIX).—5 : 6 : 7-Trimethoxyflavylium chloride (3 g.) and phenol (10 g.) were added to hydriodic acid (70 c.c.; *d* 1·7) and the mixture was gently boiled in a stream of carbon dioxide for 1 hour. In this case the salt remained in solution during the operation and we attribute the complete demethylation observed to this circumstance. After cooling, the iodide crystallised and was collected and washed with ether (yield, 1·5 g.); it formed long, transparent prisms, reddish-brown by reflected and pale brown by transmitted light. It sintered above 225° and had m. p. 254° (decomp.). The conversion into the *chloride* was carried out in dilute alcoholic solution by means of precipitated silver chloride; after concentration the salt separated in bluish-red, metallic-looking crystals (1·8 g.) and was recrystallised from 9% hydrochloric acid (500 c.c.). The glistening, dark maroon, elongated prisms with rectangular ends were dried in a vacuum over sodium hydroxide, causing them to become opaque and lustreless (Found: C, 59·6, 59·6; H, 4·0, 4·1. $C_{15}H_{11}O_4Cl,0·5H_2O$ requires C, 60·1; H, 4·0%). A specimen was boiled with hydriodic acid (*d* 1·7) and phenol for 4 hours, but no trace of methyl iodide was produced. The salt darkened above 220° and at 250—252° appeared to soften and decompose, leaving a black mass which did not melt at 320°. The chloride is sparingly soluble in water to a brownish-yellow solution and gives a reddish-brown coloration with sodium hydroxide, sodium carbonate, and

even with sodium acetate. The brownish-red alcoholic solution becomes much more intensely reddish-brown on the addition of ferric chloride.

We desire to thank the Royal Society for a grant which defrayed a part of the cost of the investigation.

THE UNIVERSITIES OF LEEDS AND MANCHESTER.

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CCCCIII.—*The Reimer–Tiemann Reaction with* m-*Bromo- and* m-*Iodo-phenol.*

By HERBERT HENRY HODGSON and THOMAS ALFRED JENKINSON.

MIXTURES of 4-bromo-2-hydroxy- and 2-bromo-4-hydroxy-benzaldehyde and of 4-iodo-2-hydroxy- and 2-iodo-4-hydroxy-benzaldehyde in almost equal quantities have been obtained by the Reimer–Tiemann reaction from *m*-bromo- and *m*-iodo-phenol, respectively, which in this respect behave like *m*-chlorophenol (this vol., p. 1740). The individual constitutions were determined by the methods previously adopted (*loc. cit.*).

Walther and Wetzlich (*J. pr. Chem.*, 1900, **61**, 198) describe a substance of m. p. 52° as either 2- or 3-bromo-4-methoxybenzaldehyde. The latter constitution appears to be correct, since the 2-bromo-compound is now found to melt at 77°.

EXPERIMENTAL.

General.—Unless otherwise stated, the methods of preparation, general properties, and crystalline form of the various products now recorded are identical with those of the chloro-analogues (*loc. cit.*). The colours produced by alcoholic alkalis on alcoholic solutions of the *p*-nitrophenylhydrazones are given immediately after the m. p.'s.

(a) *The Reaction with* m-*Bromophenol.*

4-Bromo-2-hydroxybenzaldehyde (yield, 14 g. from 67 g. of *m*-bromophenol), on being warmed with acetic anhydride and a little sulphuric acid, gives a mixture of mono- and tri-acetates. The *sodium*, *potassium*, and *copper* derivatives have been prepared. The oxime melts at 168° (Müller, *Ber.*, 1909, **42**, 3698, gives m. p. 151°) (Found : Br, 37·1. Calc. : Br, 37·0%). The p-*nitrophenylhydrazone* crystallises in orange-yellow micro-needles, m. p. 258° (decomp.); cherry-red (Found : Br, 23·7. $C_{13}H_{10}O_3N_3Br$ requires Br, 23·8%). The *semicarbazone* has m. p. 212° (Found : Br, 31·2. $C_8H_8O_2N_3Br$ requires Br, 31·0%). The *benzoate* is best prepared by gently

warming the sodium derivative (0·5 g.) with benzoyl chloride (0·3 g.), and separates from alcohol in colourless needles, m. p. 115° (Found: Br, 26·3. $C_{14}H_9O_3Br$ requires Br, 26·2%); the pyridine method of preparation (*loc. cit.*) failed.

4-*Bromo*-2-*methoxybenzaldehyde*, obtained best from 4-amino-2-methoxybenzaldehyde (*loc. cit.*), melts at 71° (Found: Br, 37·3. $C_8H_7O_2Br$ requires Br, 37·2%). *Oxime*, m. p. 132° (Found: Br, 34·8. $C_8H_8O_2NBr$ requires Br, 34·8%). p-*Nitrophenylhydrazone*, bright orange needles, m. p. 215°; violet-red (Found: N, 12·1. $C_{14}H_{12}O_3N_3Br$ requires N, 12·0%). *Semicarbazone*, m. p. 224° (Found: Br, 29·3. $C_9H_{10}O_2N_3Br$ requires Br, 29·4%). 4-*Bromo*-2-*methoxybenzoic acid*, m. p. 155° (Found: Br, 34·5. $C_8H_7O_3Br$ requires Br, 34·6%).

4-*Bromo*-2-*hydroxybenzoic acid*, colourless plates, m. p. 214° (Found: Br, 36·7. $C_7H_5O_3Br$ requires Br, 36·9%); it gives a violet colour with ferric chloride.

2-Bromo-4-hydroxybenzaldehyde (yield 15 g.; compare isomeride above) gives copper and alkali-metal derivatives. The p-*nitrophenylhydrazone* forms dark red micro-needles, m. p. 274° (decomp.); cherry-red (Found: Br, 23·6. $C_{13}H_{10}O_3N_3Br$ requires Br, 23·8%). The *semicarbazone* has m. p. 212° (Found: Br, 30·9. $C_8H_8O_2N_3Br$ requires Br, 31·0%). The oxime forms colourless needles, m. p. 184° (Gattermann, *Annalen*, 1907, **357**, 335, gives m. p. 128·5°) (Found: Br, 37·0. Calc.: Br, 37·0%).

2-Chloro-4-methoxybenzaldehyde (m. p. 62·5°. Compare Tiemann, *Ber.*, 1891, **24**, 699) and 2-*bromo*-4-*methoxybenzaldehyde*, m. p. 77° (Found: Br, 37·1. $C_8H_7O_2Br$ requires Br, 37·2%) possess hawthorn-like odours, are insoluble in water, volatile in steam, and crystallise from alcohol in long, colourless needles; the *oximes* both melt at 93° (Found: Br, 34·5. $C_8H_8O_2NBr$ requires Br, 34·8%), the p-*nitrophenylhydrazones*, orange-red needles, melt at 249° (decomp.), violet (Found: N, 13·7. Calc.: N, 13·7%), and 250° (decomp.), reddish-violet (Found: Br, 22·8. $C_{14}H_{12}O_3N_3Br$ requires Br, 22·8%), respectively; the *semicarbazones*, colourless micro-needles, melt at 240° (Found: Cl, 15·7. $C_9H_{10}O_2N_3Cl$ requires Cl, 15·6%) and 232° (Found: Br, 29·2. $C_9H_{10}O_2N_3Br$ requires Br, 29·4%). 2-*Bromo*-4-*methoxybenzoic acid*, m. p. 199° (Found: Br, 34·4. $C_8H_7O_3Br$ requires Br, 34·6%), crystallises from alcohol in short needles. 2-*Bromo*-4-*hydroxybenzoic acid* was best prepared from 3-bromo-4-nitrophenol by reduction, conversion into 3-bromo-4-cyanophenol, and hydrolysis with sulphuric acid; it crystallises from water in colourless needles, m. p. 151° (Found: Br, 36·8. $C_7H_5O_3Br$ requires Br, 36·9%), and gives a faint pink colour with ferric chloride.

(*b*) *The Reaction with* m-*Iodophenol.*

4-*Iodo*-2-*hydroxybenzaldehyde*, m. p. 87° (yield, 12 g. from 73 g. of *m*-iodophenol) is more slowly volatile in steam than its halogeno-analogues (Found: I, 51·1. $C_7H_5O_2I$ requires I, 51·2%). The *alkali-metal*, *ammonium*, and *silver* derivatives are all yellow and readily soluble in water; the green *copper* derivative is bluer than its isomeride. *Oxime*, m. p. 171° (Found: I, 48·2. $C_7H_6O_2NI$ requires I, 48·3%). p-*Nitrophenylhydrazone*, orange needles, m. p. 242° (decomp.); cherry-red (Found: I, 33·0. $C_{13}H_{10}O_3N_3I$ requires I, 33·1%). *Semicarbazone*, pale yellow needles, m. p. 252° (Found: I, 41·4. $C_8H_8O_2N_3I$ requires I, 41·6%). *Benzoate*, best prepared by the action of benzoyl chloride on the silver derivative, melts at 62° (Found: I, 36·0. $C_{14}H_9O_3I$ requires I, 36·1%).

4-*Iodo*-2-*methoxybenzaldehyde*, m. p. 85° (Found: I, 48·1. $C_8H_7O_2I$ requires I, 48·4%). *Oxime*, m. p. 138° (Found: I, 45·6. $C_8H_8O_2NI$ requires I, 45·8%). p-*Nitrophenylhydrazone*, orange-red needles, m. p. 238° (decomp.); violet-red (Found: I, 31·8. $C_{14}H_{12}O_3N_3I$ requires I, 32·0%). *Semicarbazone*, m. p. 228° (Found: I, 39·7. $C_9H_{10}O_2N_3I$ requires I, 39·8%). 4-*Iodo*-2-*methoxybenzoic acid*, m. p. 150° (Found: I, 45·9. $C_8H_7O_3I$ requires I, 45·7%), sublimes between 120° and 130° and when heated above the m. p. evolves iodine.

4-*Iodo*-2-*hydroxybenzoic acid*, colourless plates, m. p. 230° (decomp.) (Found: I, 47·8. $C_7H_5O_3I$ requires I, 48·1%); it gives a reddish-violet colour with ferric chloride.

2-*Iodo*-4-*hydroxybenzaldehyde* is odourless, non-volatile in steam, and crystallises from alcohol in very pale yellow needles, m. p. 163° (Found: I, 51·0. $C_7H_5O_2I$ requires I, 51·2%). The *alkali-metal* derivatives are yellow and the *copper* derivative is less bluish-green than its isomeride. p-*Nitrophenylhydrazone*, dark red needles, m. p. 265° (decomp.); cherry-red (Found: I, 33·0. $C_{13}H_{10}O_3N_3I$ requires I, 33·1%). *Semicarbazone*, pale yellow plates, m. p. 232° (decomp.) (Found: I, 41·3. $C_8H_8O_2N_3I$ requires I, 41·6%). *Oxime*, long, colourless needles, m. p. 155° (Found: I, 48·1. $C_7H_6O_2NI$ requires I, 48·3%). *Benzoate*, m. p. 112° (Found: I, 36·1. $C_{14}H_9O_3I$ requires I, 36·1%).

2-*Iodo*-4-*methoxybenzaldehyde* has a faint hawthorn-like odour, is volatile in steam, and crystallises from alcohol in colourless needles, m. p. 115° (Found: I, 48·5. $C_8H_7O_2I$ requires I, 48·4%). p-*Nitrophenylhydrazone*, reddish-orange needles, m. p. 247° (decomp.); reddish-violet (Found: I, 31·8. $C_{14}H_{12}O_3N_3I$ requires I, 32·0%). *Semicarbazone*, pale yellow needles, m. p. 211° (Found: I, 39·5. $C_9H_{10}O_2N_3I$ requires I, 39·8%). *Oxime*, colourless needles, m. p. 101° (Found: I, 45·6. $C_8H_8O_2NI$ requires I, 45·8%).

2-Iodo-4-methoxybenzoic acid, m. p. 184° (Found: I, 45·8. $C_8H_7O_3I$ requires I, 45·7%). *2-Iodo-4-hydroxybenzoic acid* was best prepared from 2-iodo-4-nitrotoluene; it crystallises from water (charcoal) in colourless needles, m. p. 179° (decomp.) (Found: I, 47·9. $C_7H_5O_3I$ requires I, 48·1%), and gives no colour with ferric chloride.

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CCCCIV.—*The Mechanism of the Formation of Citric and Oxalic Acids from Sugars by* Aspergillus niger. *Part II.*

By THOMAS KENNEDY WALKER, VIRA SUBRAMANIAM, and FREDERICK CHALLENGER.

THE production of citric and oxalic acids when *A. niger* is grown upon solutions containing glucose and traces of inorganic salts has been observed by many workers. In a previous communication (this vol., p. 200), it was shown that acetone, malonic acid, and glyoxylic acid can be detected in cultures of the mould on citric acid. The formation of glycollic, glyoxylic, and oxalic acids by the action of *A. niger* on calcium acetate was also established, and the suggestion was brought forward that the change glucose ⟶ citric acid ⟶ oxalic acid takes place in stages thus: glucose ⟶ gluconic acid ⟶ saccharic acid ⟶ βγ-diketoadipic acid ⟶ citric acid ⟶ acetonedicarboxylic acid ⟶ malonic and acetic acids ⟶ acetic acid (2 mols.) ⟶ glycollic acid ⟶ glyoxylic acid ⟶ oxalic acid.

Molliard, Butkewitsch, and Bernhauer have shown that gluconic acid is readily produced in cultures of *A. niger* on glucose, while both Wehmer and Schreyer have converted gluconic acid into citric acid by the further action of this or a similar mould. The present authors (*loc. cit.*) brought forward strong evidence of the formation of citric acid when *A. niger* is grown on solutions of dipotassium saccharate. It was detected by the formation of the basic mercuric sulphate compound of mercuric acetonedicarboxylate on treatment of the culture with acidified mercuric sulphate and potassium permanganate (Denigès' test, *Ann. Chim. Phys.*, 1899, **18**, 414). The citric acid was characterised as dibenzylideneacetone.

The statement of Broeksmit (*Pharm. Weekblad*, 1917, **54**, 687)

that oxidation of malic acid by potassium permanganate gives rise to acetone, detected solely by formation of iodoform with iodine and ammonium iodide, would, if correct, render identification of citric acid by this method uncertain. It is difficult to see how malic acid could yield acetone on oxidation, and on repeating Broeksmit's test a strong odour of acetaldehyde was noticed. Acetaldehyde readily gives iodoform with iodine in ammonium iodide, such a solution being no specific test for acetone.

In the case of the cultures on dipotassium saccharate it was not possible to separate the citrate as calcium salt from the large excess of saccharate (see p. 3049). Evidence of the production of acetonedicarboxylic acid (ferric chloride test) on oxidation of the contents of the culture medium was, however, obtained. When the mould is grown on potassium hydrogen saccharate solution, potassium citrate is formed in considerable amount. Further evidence of the importance of saccharic acid in the mycological production of citric acid is afforded by its isolation in the form of the potassium hydrogen salt from cultures of *A. niger* on glucose. Apart from the observation of Grüss (*Jahrbuch. wiss. Bot.*, 1926, **66**, 155, 171, 177) that saccharic acid is formed by the action of the nectar yeasts *Anthomyces Reukaufii* and *Amphiernia rubra* on glucose, this would appear to be the only recorded instance of the production of this acid by micro-organisms. Grüss identified it microscopically as the cæsium hydrogen salt.

In cultures of the nectar yeast *Microanthomyces septentrionalis* on glucose Grüss found gluconic and oxalic acids (*Woch. Brauerei*, 1927, **44**, 233).

In view of the occurrence of gluconic acid in *A. niger* cultures, and of the results just mentioned, it was to be expected that gluconic acid would yield saccharic acid by the action of the mould. This has been shown to be the case, since growth of *A. niger* on calcium gluconate solutions gives rise to calcium saccharate and some citrate. A different type of reaction was observed by Boutroux (*Compt. rend.*, 1886, **102**, 924) and by Bertrand (*Ann. Chim. Phys.*, 1904, **3**, 279), who isolated δ-ketogluconic acid from cultures of a micrococcus and of the sorbose bacteria on gluconic acid or its calcium salt. The same result was obtained by Kluyver and de Leuuw (*Tijdschrift voor vergelykende geneeskunde*, 1924, No. 10) with *Acetobacter suboxydans* and calcium gluconate.

Seekamp (*Annalen*, **1893**, **278**, 374) describes the photochemical formation of acetone from aqueous citric acid in presence of uranium oxide. In Part I of this research the formation of acetone in cultures of *A. niger* on citric acid was demonstrated and ascribed to the decarboxylation of acetonedicarboxylic acid, although proof

of its presence was lacking. By employing ammonium citrate instead of the free acid, acetonedicarboxylic acid has now been detected by the colour test with ferric chloride, and by the formation of the diphenylhydrazone of mesoxaldialdehyde on treatment of the culture with benzenediazonium chloride (von Pechmann and Jenisch, *Ber.*, 1891, **24**, 3257).

The only reference in the literature to the possible formation of this acid by a micro-organism is afforded by the observation of von Lippmann (*Ber.*, 1893, **26**, 3058; 1908, **41**, 3981) that a specimen of the calcium oxide compound of sucrose, after long keeping in a closed vessel, was converted into calcium acetonedicarboxylate. A five years old preparation had completely decomposed, giving calcium formate, acetate, oxalate and carbonate. No bacteriological examination of the products was made, but Lafar ("Handbuch der techn. Mykologie," Jena, 1908, II, 487) suggests that micro-organisms were responsible. Von Lippmann (*Ber.*, 1920, **53**, 2070) also describes the isolation of calcium malonate and calcium succinate from a solution of pure sucrose containing lime water which had become infected with bacteria, moulds, and yeasts. These observations are of interest, since malonic and acetonedicarboxylic acids have now been detected in pure cultures of *A. niger* on citric acid or a citrate. The close relations of saccharic, citric and acetonedicarboxylic acids and acetone disclosed in this research may have some bearing on the work of Wirth (*Biochem. Z.*, 1911, **33**, 49), who found that addition of gluconic, saccharic or mucic acid to blood supplied to a perfused dog's liver can lead to a decided formation of acetoacetic acid.

Oxalic acid is produced by the growth of the mould on ammonium acetonedicarboxylate, presumably by way of malonic and acetic acids, though its formation by the oxidation of "nascent" acetone produced by hydrolysis and decarboxylation is not excluded.

The tentative explanation of the mycological decomposition of citric acid suggested on p. 3044 requires the production of two molecules of acetic acid. This has not previously been detected with certainty in cultures of *A. niger* on sugars or citric acid, apart from the work of Heinze (*Ann. mycologici*, 1903, **1**, 350). This author refers to its formation in old cultures on glucose, but gives no experimental details. Acetic acid, however, may readily be isolated from ten-day cultures on citric acid, converted into acetone by dry distillation of its calcium salt, and characterised as the *p*-nitrophenylhydrazone. *B. lactis aerogenes* is stated to give rise to two equivalents of acetic acid from one of citrate (Bosworth and Prucha, *J. Biol. Chem.*, 1911, **8**, 479).

In Part I the detection of glyoxylic acid in cultures of *A. niger* on

malonic acid was described. The quantity was, however, very small, judged from the amount of the aminoguanidine derivative of glyoxylic acid which was isolated. This observation has now been confirmed, the aldehydo-acid being precipitated as the di-xanthylhydrazone (Fosse and Hieulle, *Compt. rend.*, 1925, **181**, 286), but again in very small quantity. In view of the labile nature of glyoxylic acid and its ready conversion into oxalic acid, this is perhaps not surprising. The isolation of glycollic acid from cultures of *A. niger* on calcium acetate is described in Part I. When the mould is grown upon calcium glycollate and ammonium glycollate the formation of glyoxylic and oxalic acids, respectively, may be detected, thus affording further evidence that the acetic —→ oxalic change proceeds as indicated in the scheme on p. 3044.

In Part I (this vol., 200) attention was directed to the suggestion of Franzen and Schmitt (*Ber.*, 1925, **58**, 222) that citric acid in plants is formed from saccharic acid by loss of $2H_2O$ giving rise to $CO_2H{\cdot}CH{:}C(OH){\cdot}C(OH){:}CH{\cdot}CO_2H$, which, in its keto-form, undergoes a "benzilic acid transformation," giving citric acid. The conversion of saccharic into citric acid by *A. niger* doubtless follows the same course, and is being investigated from this point of view by the authors.

Such an elimination of water from saccharic acid may possibly proceed in living organisms in a different but equally symmetrical manner, giving rise to $CO_2H{\cdot}C(OH){:}CH{\cdot}CH{:}C(OH){\cdot}CO_2H$, which by loss of carbon dioxide would yield succindialdehyde. In presence of ammonia this would form the pyrrole ring, so frequently occurring in nature. The observations of von Lippmann and of Ciskiewicz (*Ber.*, 1892, **25**, 3218; 1893, **26**, 3063) that solutions of ammonium mucate and saccharate, after spontaneous infection by atmospheric organisms, contain pyrrole are therefore of considerable interest and will be further investigated.

In view of the authors' demonstration of the biochemical significance of saccharic and acetonedicarboxylic acids, the ingredients of Robinson's synthesis of tropinone (J., 1917, **111**, 762) are seen to bear a simple relation to glucose, and the probability that similar syntheses of nitrogen compounds occur in nature (Robinson, *ibid.*, p. 880) appears to be enhanced.

Experimental.

Fermentation of Glucose. Detection of Saccharic Acid.—A medium containing glucose (300 g.), ammonium nitrate (3·2 g.), potassium dihydrogen phosphate (0·6 g.), and water (2000 c.c.) was sterilised and inoculated with a young culture of *A. niger* grown on the same

medium. A thick growth formed in 3 days at 31°. No saccharic, citric, or oxalic acid could be detected on the fourth or fifth day. On the sixth, while citric and oxalic acids were still absent, neutralisation of 150 c.c. of the culture with potassium carbonate, acidification with acetic acid, evaporation, and extraction with hot alcohol to remove glucose left a residue of about 0·2 g. of a salt giving the reactions of potassium hydrogen saccharate. Next day, traces of citric acid were detected by Denigès' test, but no oxalic acid. The whole of the solution was then neutralised and treated as before, giving 1·65 g. of a salt insoluble in alcohol, but containing much citrate. The conversion of saccharic into citric acid appears, therefore, to be very rapid after a certain phase in the development of the mould is reached. By a modification of the conditions, however, this difficulty was evaded. Twelve 300 c.c. flasks (A—L), each containing 150 c.c. of the medium, were sterilised. Six of these (A—F) were inoculated on the same day, and the remainder (G—L) after 24 hours. All were incubated at 30—32°. Growth occurred 3 days after inoculation.

Flask A was examined for saccharic, citric, and oxalic acids on the third day, flask B on the fourth day, C on the fifth, and so on. Traces of an insoluble potassium salt were isolated from C, 0·3 g. from D, and 0·8 g. from E, whilst only in E was any citric or oxalic acid to be found. After this satisfactory indication, the contents of flasks G—L were united on the sixth day after inoculation, filtered, treated with potassium carbonate and acetic acid as before, and evaporated. Repeated extraction of the residual syrup with boiling alcohol left a residue of 3·6 g. of a potassium salt. On recrystallisation from a very little hot water, this gave pure potassium hydrogen saccharate (Found: K, 15·7. Calc.: K, 15·7%. 0·0502 and 0·0461 required 20·2 and 18·5 c.c. of N/100-NaOH. Calc., 20·23, 18·57). A portion was converted into the sparingly soluble thallous hydrogen salt, and the thallium determined as thallous iodide (Found: Tl, 49·3. Calc.: Tl, 49·4%).

Fermentation of Calcium Gluconate. Detection of Saccharic Acid.—The calcium gluconate was prepared by Bert's modification of Blanchetière's method (*Bull. Soc. chim.*, 1923, **33**, 345, 733), and its purity checked by determinations of calcium (Found: Ca, 9·3. Calc.: Ca, 9·3%) and the specific rotation, $[\alpha]_D$ + 7·7°. The medium contained water (1000 c.c.), calcium gluconate (20 g.), and the usual mineral salts in the proportions contained in Molliard's solution M (this vol., pp. 202—204). Inoculation with mycelium from a 200 c.c. culture gave growths on the fourth day at 31°. On the next day the solution was filtered, concentrated to 800 c.c. under diminished pressure, and boiled; a precipitate containing calcium

citrate (1·2 g.) then separated. Further boiling produced no deposit and the filtrate was concentrated in a vacuum to 350 c.c. On cooling, a white solid (3·7 g.) separated which was free from citrate. It was recrystallised twice with difficulty from much hot water (calcium saccharate is sparingly soluble) and dried ove r sulphuric acid (Found : Ca, 16·0. Calc. : Ca, 16·1%).

0·7 G. was boiled with 0·5 g. of potassium carbonate in 10 c.c. of water, and the filtrate acidified with acetic acid. The resulting potassium hydrogen saccharate was recrystallised twice from hot water (0·0623 and 0·0712 required 25·0 and 28·7 c.c. of $N/100$-NaOH. Calc., 25·13, 28·8), and a portion of it then converted into thallous hydrogen saccharate (Found : Tl, 49·3. Calc. : Tl, 49·4%).

Fermentation of Dipotassium Saccharate. Detection of Citric Acid.—A solution containing 40 g. of the normal potassium salt in 2000 c.c. of solution M was sterilised and inoculated. After 28 days at 31° the presence of citric acid was detected by Denigès' test. 5 G. of the evaporated culture were oxidised by hot 2% potassium permanganate solution in presence of acidified mercuric sulphate solution, giving a white solid. A few grams of this were washed, suspended in water, and treated with hydrogen sulphide. The filtrate from the mercury sulphide was repeatedly extracted with ether, and the wet solvent evaporated under diminished pressure. The slight aqueous residue gave a reddish-purple coloration with ferric chloride, similar to that produced by acetonedicarboxylic acid, thus confirming the presence of a citrate (Denigès, *Ann. Chim. Phys.*, 1899, **18**, 408, 414). This reaction was not due to the presence of the keto-acid in the original culture, as this would have been decomposed during evaporation. Only a trace of a precipitate was obtained with mercuric sulphate before oxidation with permanganate, and this was removed.

Attempts were then made to precipitate calcium citrate from the culture, but the presence of the saccharate had a disturbing effect. Normal calcium saccharate is very sparingly soluble in water, but soluble in excess of calcium chloride. This solution gives no precipitate on boiling, even on evaporation to a small bulk. When citrate is present, however, the clear solution gives a precipitate when boiled which contains saccharate and citrate, no separation being effected. When a mixture of dipotassium saccharate and potassium citrate is treated in the cold with calcium chloride approximately equivalent to the saccharate, the resulting precipitate contains both saccharate and citrate. The filtrate on boiling deposits calcium saccharate.

When insufficient calcium chloride is added the initial precipitate of calcium saccharate redissolves. On boiling the clear solution,

successive deposits are obtained which contain saccharate, citrate being present in some cases.

In other experiments, the saccharic acid was partly removed as the potassium hydrogen salt by addition of acetic acid to the concentrated culture, and the filtrate was neutralised with potassium carbonate, treated with calcium chloride, and boiled. Calcium citrate was not precipitated and it was then found that excess of sodium acetate greatly retards the precipitation of this salt from hot solutions. The effect of salts of other organic acids on the precipitation of calcium citrate appears to have received very little attention.

Fermentation of Potassium Hydrogen Saccharate. Detection and Isolation of Citric Acid.—The mould grew more readily on solutions of the potassium hydrogen salt than on those of the normal salt. A mixture of solution M (2000 c.c.) and potassium hydrogen saccharate (40 g.) was sterilised, inoculated and incubated at 31°. On the fourteenth day citric acid was detected by Denigès' reagent (*loc. cit.*, p. 384), whereupon the remainder of the solution (1800 c.c.) was filtered, concentrated under diminished pressure, and evaporated, leaving 36 g. of moist residue. A duplicate experiment yielded 34 g. The residues were united and heated under reflux for 1 hour with 400 c.c. of 65% alcohol (in which potassium hydrogen saccharate is insoluble, but potassium citrate is easily soluble), and the solution was filtered and evaporated. The residue was converted into the lead salt, which was decomposed by hydrogen sulphide, and the filtrate from the lead sulphide was decolorised with charcoal and evaporated (3·6 g.). After three crystallisations from dry ether–light petroleum, its m. p., alone or in admixture with anhydrous citric acid (m. p. 153°), was 153·5° (0·1212 and 0·0560 required 37·7 and 17·5 c.c. of *N*/20-NaOH. Calc., 37·8, 17·5. Found: C, 37·5; H, 4·7. Calc.: C, 37·5; H, 4·2%). A portion was neutralised with potassium hydroxide and treated with thallous nitrate, and the resulting thallium salt was twice crystallised from hot water and analysed (Found: Tl, 76·4, 76·6. Calc.: Tl, 76·4%).

Fermentation of Ammonium Citrate. Detection of Acetonedicarboxylic Acid.—A medium containing ammonium citrate (20 g.) and citric acid (4 g.) in solution M (2000 c.c.) was inoculated from test-tube cultures, growth occurring on the third day at 31°. On the third, fourth, and fifth days 50 c.c. of the culture were removed, filtered, and treated with 3 g. of sodium acetate, and a benzenediazonium chloride solution (prepared from 0·3 g. of aniline) was added at 0°. On the fifth day, a red coloration was observed after 3 hours. A further 10 c.c. of the culture were shaken with 50 c.c. of cold Denigès' mercuric sulphate solution, a white precipitate being

obtained. (Acetone in dilute solution gives a precipitate only on warming.) These two tests were regarded as indications of the probable presence of acetonedicarboxylic acid.

At this stage 1800 c.c. of the filtered culture were treated with corresponding proportions of benzenediazonium chloride solution and sodium acetate at 0°. A red precipitate formed in 8 hours. This was separated, washed with ice-water, dried (1·3 g.), washed with light petroleum, and recrystallised from alcohol and then from ethyl acetate; it then melted at 175°, and at 175—176° in admixture with the diphenylhydrazone of mesoxaldialdehyde (m. p. 175—176°) prepared from acetonedicarboxylic acid and benzenediazonium chloride (Found: N, 21·3. Calc.: N, 21·1%). Both specimens gave a deep violet coloration with sulphuric acid (Bülow reaction).

Fermentation of Citric Acid. Detection of Acetic Acid.—The medium employed contained 3·5 g. of citric acid in 4000 c.c. of solution M. After sterilisation it was inoculated with 700 c.c. of a three days' culture of *A. niger* on the same medium. Growth was observed on the third day at 31°. 50 C.c. of the culture were then withdrawn on successive days and carefully distilled in steam and the volatile acids were determined. On the third and fourth days, 0·4 c.c. of *N*/20-sodium hydroxide was required, on the seventh 3·8 c.c., ninth 10·2, tenth 11·8, eleventh 11·9, twelfth 11·0. The whole of the culture was then filtered, neutralised with sodium carbonate, concentrated in a vacuum to 100 c.c., acidified with phosphoric acid, and carefully distilled in steam till the distillate was no longer acid (200 c.c.). This was neutralised with sodium carbonate and evaporated and the residue (2·8 g.) was extracted with 15 c.c. of 95% alcohol, in which sodium acetate is soluble. The residue (0·4 g.) contained no formate. The alcoholic extract was evaporated; the residue, which appeared to be sodium acetate, was converted into the silver salt, which was crystallised twice from hot water and dried (Found: Ag, 64·4, 64·8. Calc.: Ag, 64·7%). A further portion of the sodium salt was distilled with phosphoric acid, the distillate neutralised with calcium carbonate, and the dry calcium salt distilled, giving a few drops of liquid, which were warmed with 30 c.c. of Denigès' mercuric sulphate solution (Part I, p. 206). The resulting precipitate (2·8 g.) was separated and decomposed by distillation with 5 g. of sodium iodide and 10 c.c. of water, and the distillate was collected in a solution of *p*-nitrophenylhydrazine acetate (Part I, p. 207). Long, yellow needles separated in 3 hours which, recrystallised from alcohol, melted at 148·5° and did not depress the m. p. (148·5°) of an authentic specimen of acetone-*p*-nitrophenylhydrazone.

Malonic acid also is a product of the fermentation of citric acid

by *A. niger*. In order to exclude the possibility that the acetic acid arose by the decarboxylation of this acid (normally occurring at 140°) a mixture of 100 c.c. of solution M, 1 g. of citric acid, and 1 g. of malonic acid was distilled in steam. The distillate was not acid.

Fermentation of Ammonium Acetonedicarboxylate. Detection of Oxalic Acid.—The medium contained the ammonium salt (20 g.) in solution M (2000 c.c.). It was prepared and sterilised as in the case of the ammonium glycollate solution, inoculated, and incubated at 32°. Oxalate was found on the eighteenth day by removing 20 c.c., boiling with dilute hydrochloric acid to decompose the keto-acid (which gives a sparingly soluble calcium salt), neutralising the solution with ammonia, and adding calcium chloride.

The main bulk was then treated in a similar manner, complete decomposition of the keto-acid being indicated by the absence of a precipitate with Denigès' solution, which detects 1 part of acetonedicarboxylic acid in 5000 parts of water. The calcium oxalate was dissolved in hydrochloric acid, reprecipitated, and dried (1·6 g.) (Found: Ca, 31·2. Calc.: Ca, 31·25%. 0·1436 required 44·9 c.c. of $N/20$-$KMnO_4$. Calc., 44·87).

Fermentation of Malonic Acid. Detection of Glyoxylic Acid.—The medium contained 20 g. of malonic acid in 2000 c.c. of solution M. It was inoculated with mycelium from a smaller culture on the same medium and incubated at 31°. On the seventeenth day a positive reaction for glyoxylic acid was obtained with naphtharesorcinol. 1000 C.c. of the filtered culture were treated with 1 c.c. of 50% hydrazine hydrate and then with 4 g. of xanthhydrol dissolved in 1000 c.c. of glacial acetic acid. After addition of water and shaking, the precipitate was separated, and centrifuged with a slight excess of alcoholic N-sodium hydroxide; by this means any trixanthylhydrazine remains insoluble. The clear liquid was decanted and treated with acetic acid, and the pale pink crystalline precipitate was recrystallised twice from chloroform–light petroleum (0·5 g.). After drying in a vacuum over calcium chloride, it melted at 146·5°. In admixture with an authentic specimen of the dixanthylhydrazone of glyoxylic acid (m. p. 147°) it melted at 146·5°.

A blank experiment was carried out on the unfermented medium, but no precipitate was obtained on acidification of the alkaline alcoholic extract.

Fermentation of Malonic Acid. Detection of Oxalic Acid.—A sterilised solution containing 25 g. of malonic acid in 2500 c.c. of solution M was inoculated and incubated at 30°. On the eighteenth day oxalate was detected on addition of calcium chloride to the cold solution, whereupon 800 c.c. were withdrawn, filtered, concentrated

in a vacuum to 400 c.c., and neutralised with ammonia, and excess of 10% calcium chloride solution was added. The precipitate was redissolved in dilute hydrochloric acid and reprecipitated with ammonia (Found : Ca, 31·3, 31·2. Calc. : Ca, 31·25%. 0·0832 and 0·0976 required 25·9 and 30·10 c.c. of $N/20$-$KMnO_4$. Calc., 26·0, 30·5). (Under the experimental conditions any glyoxylic acid would be partly converted into oxalic acid.)

Glyoxylic acid or its ammonium salt in 2% aqueous solution gives no precipitate with cold calcium chloride unless the solution has been boiled and again cooled, calcium oxalate then being precipitated.

Fermentation of Calcium Glycollate. Detection of Glyoxylic Acid.— The medium contained 40 g. of calcium glycollate in 4000 c.c. of solution M. The water was first sterilised and the glycollate added. The solution gave no test for glyoxylic acid and was inoculated with mycelium from four test-tube cultures on the same medium and incubated at 22°. On the sixth day a mixture of 10 c.c. of the medium, 10 c.c. of hydrochloric acid, and a trace of 1 : 3-dihydroxynaphthalene was boiled for 1 minute, cooled to 16°, and extracted with ether, which acquired a purple colour (naphtharesorcinol test) indicating the presence of glyoxylic acid or a similar compound.

On the twenty-seventh day 1800 c.c. of the culture were treated with 7 g. of aminoguanidine acetate, giving after 3 days a yellow deposit (0·3 g.). On recrystallisation from hot water this had m. p. 155° and did not depress the m. p. (155°) of an authentic specimen of the aminoguanidine derivative of glyoxylic acid.

A further 1800 c.c. of the filtered medium were treated with 1 c.c. of 50% hydrazine hydrate and then with 4 g. of xanthhydrol in 1800 c.c. of glacial acetic acid (a blank experiment was carried out on 1800 c.c. of acetic acid) (see p. 3052). On addition of water a white precipitate was produced. This was separated after an hour, dried, and treated with alcoholic N-sodium hydroxide. The resulting solution was filtered and acidified with acetic acid, and the precipitate was washed with aqueous alcohol, dried over soda–lime, and twice crystallised from chloroform–light petroleum; it then melted at 147° and did not depress the m. p. (147°) of an authentic specimen of the dixanthylhydrazone of glyoxylic acid (Found: C, 71·8; H, 4·85. Calc. : C, 72·1; H, 4·7%). The acetic acid used as solvent was shown to be free from glyoxylic acid both by the naphtharesorcinol and by the xanthhydrol test.

Fermentation of Ammonium Glycollate. Detection of Oxalic Acid.— The medium contained 20 g. of ammonium glycollate in 2000 c.c. of solution M. It was not sterilised in the usual manner, the glycollic acid being dissolved in sterile water, almost neutralised with am-

monia and diluted with sterile water. Inoculation was effected with 200 c.c. of a smaller culture on the same medium. On the tenth day 1800 c.c. of the culture were filtered, treated with a slight excess of 10% calcium chloride solution, warmed, and filtered. The precipitate was dissolved in hydrochloric acid and reprecipitated with ammonia (2·9 g.) (Found: Ca, 31·2. Calc.: Ca, 31·25%. 0·1237 required 38·6 c.c. of $N/20$-$KMnO_4$. Calc., 38·65).

The cost of this investigation has been in part defrayed by a grant from the Government Grant Committee of the Royal Society. A State Scholarship awarded to one of us (V. S.) by the Ministry of Development, Government of Madras, has enabled him to participate in the research. To both of these bodies the authors wish to express their thanks, and also to Mr. P. D. Coppock, M. Sc., for carrying out the fermentation of calcium glycollate and the analysis of the products.

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CCCCV.—*The Influence of Alkalis on the Coagulation of Silica and Clay Suspensions by Alkali Chlorides.*

By HENRY BOWEN OAKLEY.

MANY studies have been made on the coagulation of clay suspensions and silicic acid sols by electrolytes, but hardly any systematic observations have been made on the influence of the reaction of the medium on the results, although Bradfield (*J. Amer. Chem. Soc.*, 1923, **45**, 1243) has shown that this factor has a great influence on the coagulation of clay, as on most other aqueous colloidal systems.

In continuance of the comparison of the properties of clay and silica made in these laboratories, a comparative study of the coagulation of a fine suspension of the latter substance was also made. The results suggested that silica on which small quantities of alumina had been precipitated might behave like clay in its coagulation by mixtures of alkali-metal chlorides and hydroxides. This proved to be the case when certain conditions were observed, and the general results lend further support to the view that the reactions involved in the absorption of alkalis by clay and its coagulation are of a chemical nature. The experiments recorded in this paper are confined to the alkali-metal and calcium chlorides and hydroxides.

Description and Preparation of Clay.—The clay used in these

experiments was No. 10195, prepared from a heavy cotton soil by decantation from 0·05% sodium carbonate. It was flocculated by dilute hydrochloric acid ($N/100$) and purified to a high resistance by dialysis. The molecular ratio $SiO_2 : Al_2O_3$ was about 4. The clay was practically identical with No. 6640 described by Joseph and Hancock (J., 1924, **125**, 1888) and contained 0·15% of humus. It may be objected that the process of purification may largely alter the characteristics of clay; this is certainly true in that an "acid" clay has very different properties from the same clay combined with a base, but there is no evidence that the process of purification alters the clay in any other way.

Experimental.

The Nephelometric Method of Measuring the Concentration of Clay Suspensions.—In some of the experiments the amount of clay remaining in suspension in the various tubes after 1 hour was estimated by comparison with a standard suspension of clay in a Klett nephelometer. Preliminary experiments showed that, contrary to expectation, neutral flocculants even in excess did not affect the turbidity if the suspension was stirred immediately before the measurement was made. The addition of alkalis, however, produced a very marked decrease in turbidity, the effect apparently being dependent only on the nature of the alkali and not on its concentration. The following table shows the effect produced by hydroxides and carbonates, the turbidity of a 0·1% purified clay suspension being taken as unity and used as standard.

	Ba.	Ca.	NH_4.	K.	Na.	Li.
Hydroxide	0·95	0·93	0·84	0·81	0·58	—
Carbonate	—	—	0·82	0·84	0·64	0·50

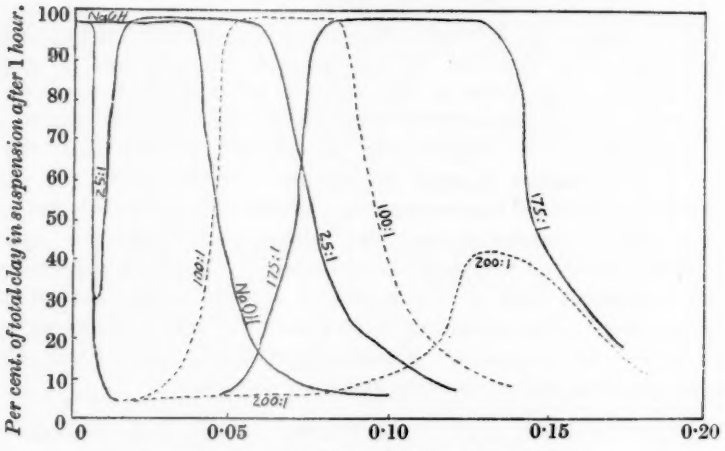
The order is approximately that of the Hofmeister series. This decrease in turbidity was allowed for in measuring the concentration of alkaline suspensions by using an alkaline standard.

The Flocculation of Clay by Mixtures of the Chlorides and Hydroxides of the Alkali Metals.—Following Bradfield (*loc. cit.*), a series of mixtures was prepared, N with respect to sodium, containing sodium chloride and sodium hydroxide in ratios ranging from 2 : 1 to 200 : 1. Each mixture was added in increasing amounts to a series of large boiling-tubes. Water was added to make the volume up to 45 c.c., and then 5 c.c. of a 1% suspension of purified clay (10195) were added at 5-minute intervals to each tube. These were shaken a dozen times by hand, and after standing undisturbed for 1 hour, 10 c.c. were withdrawn with a pipette 3·5 cm. below the surface. The height of each column of liquid was about 7 cm.

The amounts of clay in these samples were estimated in the nephelometer, and when required, the p_H of a further sample was also measured electrometrically with a Clark's cell.

Some of the results are plotted in Fig. 1. The ordinates represent the percentage of the total amount of clay remaining in suspension after 1 hour and the abscissæ the total concentration of the sodium. The interesting effect is observed that the curves for mixtures in which the ratio of chloride to hydroxide is 25 to 1 or more show a pronounced maximum and minimum, the range of the latter increasing with increasing ratio of chloride to hydroxide, until with pure sodium chloride the maximum has disappeared completely. This

FIG. 1.



Concentration of sodium added (equiv. per litre).

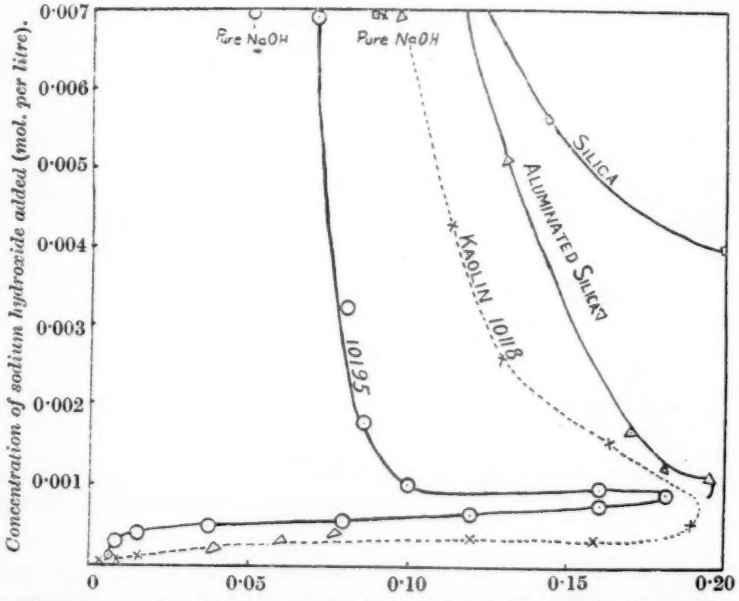
Ratios represent that of NaCl : NaOH.

phenomenon has been observed with different clays and only fails when the initial reaction of the suspension is alkaline (*Nature*, 1926, **117**, 624). It is also shown with a more limited range of mixtures by kaolin, but here the ratio of chloride to hydroxide must not be less than 250 to 1. The same phenomenon is shown with lithium, potassium, and also calcium at much lower concentrations and for mixtures in which the ratio of calcium chloride to calcium hydroxide varies from 1 : 1 to 3 : 1.

The following scheme compares the effects of mixtures of potassium, sodium, and lithium chlorides with their respective hydroxides in which the ratio of chloride to hydroxide is 100 : 1. A minus sign indicates no flocculation in 1 hour, and a plus sign indicates that less than 30% remains in suspension after 1 hour.

Conc. of metal, × 10^3.	K.	Na.	Li.	Ca (conc. × 10^4). $CaCl_2 : Ca(OH)_2 = 2 : 1$.
2	−	−	−	−
3	+	−	−	−
5	+	−	−	−
7	+	+	−	−
10	+	+	+	−
20	+	+	+	−
30	+	+	+	−
40	±	−	−	−
50	−	−	−	−
60	−	−	−	−
80	+	−	−	+
100	+	±	−	+
140	+	+	−	−
180	+	+	+	−
200	+	+	+	+

FIG. 2.

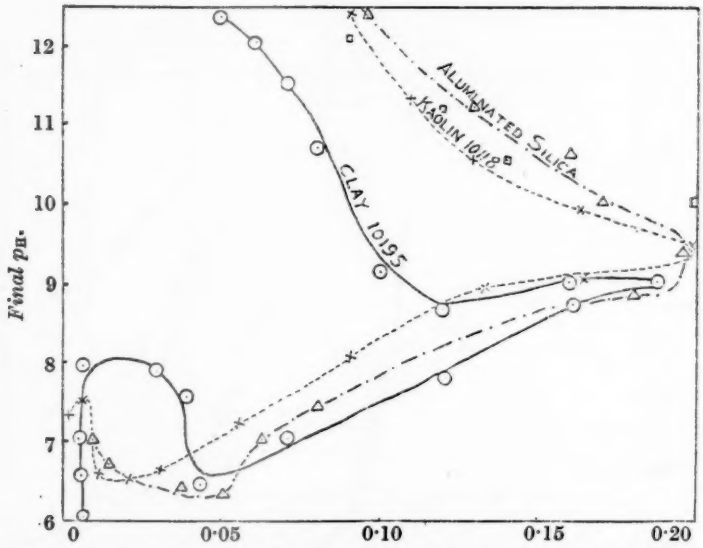


Minimal concentration of sodium (equiv. per litre) for flocculation in **1** *hour.*

It will be noticed that the flocculating power and the first zone of coagulation decrease in passing from potassium to lithium. This phenomenon was not observed by Bradfield (*loc. cit.*), who worked on the finest fraction of clay separated by means of a supercentrifuge. His suspension, although acid, had not been treated with *N*/100-hydrochloric acid before purification, as in the present work, and his observations were made after the suspensions had been standing for 24 hours.

The influence of the alkalinity on the minimal concentration of kation required to flocculate clay in 1 hour can best be summarised by plotting these quantities. In Fig. 2, the concentration of hydroxide added is plotted against this minimal concentration, and in Fig. 3 the final p_H is similarly plotted. The minimal concentration is defined, for the purpose of these curves, as that concentration which allows between 20 and 40% of the clay to remain in suspension after 1 hour. The results for kaolin and for silica on which a small quantity of aluminium hydroxide has been precipitated are also included in these diagrams, and will be discussed later. The most

FIG. 3.

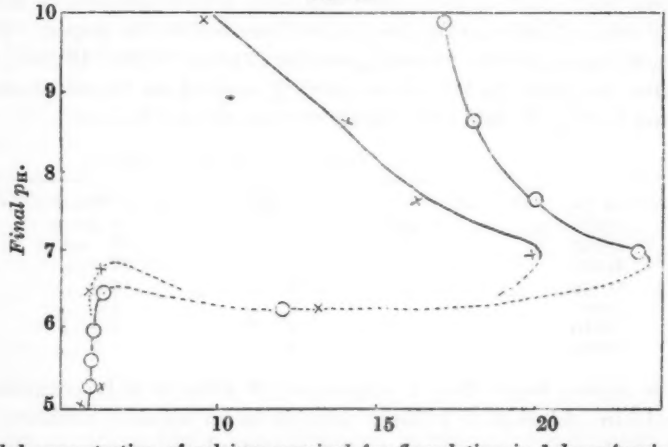


Minimal concentration of sodium (equiv. per litre) for flocculation in 1 hour. Squares represent silica.

important characteristic of these curves is that the minimal concentration of sodium required for flocculation rises very rapidly on the addition of small quantities of alkali, and reaches a very pronounced maximum when the concentration of alkali added is $0{\cdot}009N$ or when the p_H is 9. This for a 0·1% suspension corresponds to the amount of sodium this clay can absorb without beginning to break down into soluble silicates and aluminates (Oakley, this vol., p. 2819). A curious feature of the curves in Fig. 3 is the sudden drop in the p_H and its subsequent rise with increasing concentrations of sodium, and this in spite of the steadily increasing concentrations of alkali as shown in Fig. 2. Although the measurements in this

neighbourhood are admittedly difficult to repeat, there is no doubt of the reality of the effect which has been observed in each of the three substances studied. The fall in p_H is due to increased absorption of sodium with increasing sodium-ion concentration accompanied by the liberation of an equivalent quantity of hydrogen ions. The combination of the clay with sodium is accompanied by an increase in the concentration of sodium ions required to flocculate it in a given time. That sodium chloride has a very large effect in decreasing the p_H of clay suspensions is shown by the following figures. The effect is far greater than that produced on sodium silicate which is in true solution, and it is generally agreed that this is due to the

FIG. 4.



Added concentration of calcium required for flocculation in 1 hour (equiv. per litre $\times 10^4$*) (circles). Specific conductance* ($\times 10^5$) *at 20° (crosses).*

combination of sodium with the clay acid, with the liberation of an equivalent quantity of free acid.

The lowering of p_H by the addition of neutral salt.

1% Clay suspension.		Sodium silicate ($SiO_2 = 0{\cdot}02M$).	
No NaCl.	$N/2$-NaCl.	No NaCl.	$N/2$-NaCl.
10·70	9·30	10·72	10·39
10·01	7·85	9·90	9·62
9·40	7·00	9·40	9·00
8·60	6·30	—	—

The Flocculation of Clay by Calcium Chloride and Hydroxide.—These results are plotted in Fig. 4; as with sodium, the minimal concentration of calcium required for flocculation shows a sudden increase to a maximum with the addition of small quantities of calcium hydroxide, but here the concentrations are about 1/10 of

those for sodium, and the p_H at the maximum is 7 instead of 9. The curve for the specific conductivity shows that the decrease in the minimal concentration above a p_H of 7 is even more marked than that indicated by the other curve, which shows the initial concentration of calcium added. As with sodium, the results indicate that the combination of the clay with calcium in the initial stages is accompanied by an increase in the concentration of calcium ions required to flocculate it in 1 hour. This is directly opposite to the results obtained by Comber (*J. Agric. Sci.*, 1920, **10**, 425) and confirmed by Kermack and Williamson (*Nature*, 1926, **117**, 824), who found that clay was more readily flocculated by calcium in an alkaline medium. The discrepancy is due to the fact that these workers used more concentrated solutions and consequently much higher rates of flocculation than those described in this paper. This is clearly shown by the following results (*Nature*, 1926, **118**, 661) for the time required to flocculate a 0·1% suspension in solutions of calcium hydroxide and chloride at various concentrations.

	Time required for flocculation.		
Conc. of $Ca^{..}$ ions.	$Ca(OH)_2$.	$CaCl_2$.	$2Ca(OH)_2 + CaCl_2$.
0·001	7 hours	14 mins.	6 hours
0·002	28 mins.	10 „	32 mins.
0·003	2 „	7 „	12 „
0·004	1·5 „	6 „	4·5 „
0·005	1·5 „	6 „	3·5 „
0·010	1·5 „	6 „	1·5 „
0·014	1·5 „	6 „	1·5 „

It is shown below that a suspension of silica is only coagulated by calcium chloride or sodium chloride in an *alkaline* medium. I suggest that the reason why clay is coagulated more readily in an alkaline medium only when the concentration of the alkali is above a certain value is that at these higher concentrations some of the clay is broken down into silicates (Oakley, *loc. cit.*) and thus behaves in flocculation like silica.

The Effect of Alkalis on the Flocculation of Silica.—Smith (*J. Amer. Chem. Soc.*, 1920, **42**, 461) noticed that silicic acid is coagulated by sodium and calcium hydroxides at concentrations of 0·1 and 0·002, respectively, but not at all by the chlorides at a concentration of 0·07. These results have been confirmed for a silica suspension. The silica used in these experiments was purified by repeated treatments with hot concentrated hydrochloric acid, washed by decantation, and dialysed to a high specific resistance. It was then reduced to a finely divided state by repeated grinding in a wet condition in an agate mortar and sedimentation. In this way, a 1% suspension was obtained which remained in suspension for 2 hours. The following table gives the minimum concentration of

sodium required to cause coagulation of a 0·1% suspension in 1 hour, various mixtures of sodium chloride and sodium hydroxide being used. The experiments were made in test-tubes, the volume being 10 c.c., and 1 c.c. of the 1% suspension being added last.

The flocculation of silica by sodium chloride and hydroxide mixtures.

NaCl : NaOH.	Conc. NaOH, ×100.	Conc. Na, ×100.	p_H.	NaCl : NaOH.	Conc. NaOH, ×100.	Conc. Na, ×100.	p_H.
0 : 1	9·0	9	12·21	300 : 1	0·14	42	9·21
10 : 1	1·2	12	11·13	500 : 1	0·11	55	8·73
25 : 1	0·56	14	10·53	1000 : 1	0·07	70	8·20
50 : 1	0·40	20	10·06	2000 : 1	0·045	90	7·27
100 : 1	0·26	26	9·77	1 : 0	0·00	100	No flocc.
200 : 1	0·18	37	9·54				

Some of these results are plotted in Figs. 2 and 3. Above a p_H of 10, the points for silica lie close to the curve for kaolin, but with a decrease in the p_H the flocculating concentration for silica continues to increase rapidly, whereas for kaolin and clay it shows a sudden decrease.

The Flocculation of Silica by Alumina.—It was thought that this difference in the flocculating concentrations for clay and silica might be connected with the presence of combined alumina in the former substance, and it was accordingly decided to precipitate small quantities of alumina on silica and to find out how this product behaved towards coagulation by mixtures of sodium chloride and hydroxide.

In the following experiments the effect of sodium hydroxide on the coagulation of silica by aluminium chloride was studied. The order of adding the reagents has an effect. In these experiments the 1% silica suspension was always added to the aluminium chloride solution, and the sodium hydroxide was added last. The final concentration of silica was 0·1%. The following scheme summarises the results. The sign of the charge of the resultant suspension was determined by cataphoresis in a U-tube.

Flocculation of a 0·1% silica suspension by aluminium chloride and sodium hydroxide.

$AlCl_3$ (mol. per litre).	NaOH (mol. per litre).	Sign of charge.	Whether flocculated or not.	p_H.
<0·0001	0	—	Deflocculated	
0·0001	0	Neutral	Flocculated slowly	2·4
>0·0001	0	+	Deflocculated	
0·0001	<0·0002	Neutral	Flocculated slowly	
0·0001	0·0002	Neutral	Flocculated	5·3
0·0001	>0·0002	—	Deflocculated	
0·001	<0·003	+	Deflocculated	
0·001	0·003	Neutral	Flocculated	8·5
0·001	>0·004	—	Deflocculated	

Small quantities of aluminium chloride flocculate silica, but larger quantities give a stable electropositive suspension. The addition of sodium hydroxide in quantities approximately equivalent to the aluminium chloride rapidly flocculates the silica, but the p_H at which this most rapid flocculation takes place depends on the concentration of aluminium chloride. The further addition of sodium hydroxide results in the formation of a stable electronegative suspension. I think these results are most simply accounted for by supposing the particles of the electropositive suspensions to be coated with aluminium hydroxide, which therefore imparts the properties of a suspension of this substance to the silica. Thus, like aluminium hydroxide, it is electropositive and is easily flocculated by the addition of sodium hydroxide. With the further addition of caustic soda, a surface layer of sodium aluminosilicate is formed, which, like clay, is electronegative owing to surface ionisation into sodium ions and insoluble aluminosilicate ions. This substance should therefore behave like clay with regard to flocculation by mixtures of sodium chloride and hydroxide.

The Preparation and Flocculation of "Aluminated" Silica.—A stock of silica coagulated with aluminium hydroxide was prepared by adding to a 1% suspension of silica, water, aluminium chloride, and then sodium hydroxide in amounts to make the final concentrations 0·5% of silica, 0·001*M*-aluminium chloride and 0·0023*N*-sodium hydroxide. To obtain coagulation, it was necessary to determine these concentrations with some care by making initial trials on small quantities. The suspension was centrifuged, the supernatant liquid decanted, and water added to the residue to make the suspension 1%. This was stable when diluted to 0·1%. The settled material was about four times as bulky as silica. A series of flocculation experiments using mixtures of sodium chloride and hydroxide was then made on 0·1% suspensions in test-tubes as with silica : the results are plotted as triangles in Figs. 2 and 3. An exactly similar series of observations was made on a pure suspension of kaolin : these results are shown as crosses in the figures. The curves for the two substances have closely similar characteristics, although the maximum in both cases is less pronounced than for clay.

Both "aluminated" silica and kaolin showed successive flocculation, deflocculation, and flocculation on the addition of increasing quantities of alkaline sodium chloride, provided the ratio of chloride to hydroxide was not less than 250 : 1. Silica, however, does not show this phenomenon. The following scheme compares the behaviour of the three substances towards flocculation by a 300 : 1 mixture of sodium chloride and hydroxide. The negative sign

indicates no flocculation and the positive sign flocculation after 1 hour. It should be mentioned that these results were obtained on a suspension of "aluminated" silica only 2 or 3 days old; a few experiments on a preparation which had been standing several months showed a change in the concentrations required for flocculation.

Conc. of $Na^{\cdot}$ ion, $\times 10^3$.	Silica.	"Aluminated" silica.	Kaolin (10118).
3	−	−	−
5	−	−	+
7	−	+	+
10	−	+	+
15	−	+	+
20	−	+	−
30	−	+	−
40	−	−	−
50	−	−	−
70	−	+	−
100	−	+	−
150	−	+	−
180	−	+	+
450	+	+	+

Comparison of the Flocculating Powers of Sodium Hydroxide, Carbonate and Bicarbonate.—As might be anticipated from the curves in Fig. 3, sodium hydroxide flocculates at a lower concentration than the carbonate, which in turn flocculates at a lower concentration than the bicarbonate, since this is the order of decreasing alkalinity of the three compounds. This is illustrated in the following table:

Concentration of alkali required to flocculate in 1 hour.

Clay.	NaOH.	Na_2CO_3.	$NaHCO_3$.
Gezira (10195)	0·05	0·30	0·35
Mongalla (18107) (red)	0·21	0·32	0·32
Kaolin (10118)	0·09	0·40	0·42
Silica	0·09	0·42	0·95
"Aluminated" silica	0·09	0·25	0·60

In the present paper, I have purposely omitted any discussion of the mechanism of flocculation, owing to the absence of any really satisfactory theory of the phenomenon for colloids in general, but I think that the maxima and minima in the curves of Fig. 1 can be regarded as the outcome of two opposing factors in the stability of clay. The first factor, which tends to stabilise the suspension, is the formation of a sodium compound with the clay; the extent to which this takes place will depend upon the reaction of the medium and the concentration of sodium ions, and reaches a limit between p_H 9 and 10 (Oakley, *loc. cit.*). The second factor, which tends to flocculate the suspension, is the concentration of electrolyte in solution. With increasing concentrations of slightly alkaline

sodium chloride, the clay is first flocculated at a low concentration because it remains essentially an "acid clay" and contains no sodium to stabilise it. With higher concentrations, sodium is absorbed in increasing quantities until the sodium–clay complex is sufficiently lyophilic to withstand quite high concentrations of sodium chloride, but the concentration at which this second deflocculation takes place will depend on the alkalinity of the mixture used, being lower the greater the concentration of alkali until, with strongly alkaline mixtures, sodium–clay compounds are formed from the start and no minimum occurs in the flocculation curve. The deflocculated sodium clay is finally flocculated by increasing concentration of electrolyte.

With regard to the mechanism of flocculation, the theory of mutual electrical repulsion between the particles is very inadequate, as McBain has pointed out (*Colloid Symposium Monograph*, 1926, **4**, 13). I think the views put forward by Duclaux (*J. Chim. phys.*, 1909, 405) on the importance of osmotic forces in colloidal solutions and suspensions offer the most hopeful starting point in the development of an adequate theory of their stability.

Summary.

1. Certain mixtures of sodium, potassium, lithium, or calcium chloride with the respective hydroxide, when added in increasing amounts to a purified clay suspension, at first flocculate, then fail to flocculate, and finally flocculate the clay again. The phenomenon is shown by kaolin and also by silica coagulated by a small quantity of alumina, but not by pure silica, and it fails only when the suspensions are alkaline. The flocculating powers are in the increasing order: lithium, sodium, potassium, calcium, the last being about 10 times as powerful as sodium.

2. There is a pronounced maximum between a p_H of 9 and 10 in the concentration of sodium or calcium chloride required to flocculate clay or kaolin. The "aluminated" silica is remarkably similar to kaolin in respect of the influence of alkalis on the concentration of sodium chloride required for flocculation, and both these substances have similar characteristics to clay with regard to flocculation.

3. Silica is flocculated by sodium or calcium chloride only when the medium is alkaline. The minimal concentration required for flocculation rises rapidly as the alkalinity diminishes.

4. Silica is flocculated by 0·0001*M*-aluminium chloride; greater concentrations give a stable electropositive suspension. The subsequent addition of small quantities of sodium hydroxide at first flocculates the suspension and then gives a stable electronegative suspension.

5. Clay is more readily flocculated by calcium hydroxide than by calcium chloride at equivalent concentrations provided the concentration exceeds 0·003*N*. Below this concentration calcium chloride is the better flocculant.

I wish to express my appreciation of the helpful interest of Dr. A. F. Joseph in this work.

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KHARTOUM. [*Received, June 29th*, 1927.]

CCCCVI.—*The Interaction of Bromine with Acetic Anhydride. Part III. Arrest of the Reaction. A Comparison with the Bromination of Acetone.*

By HERBERT BEN WATSON.

THE powerful negative catalytic effect of quinoline and the less marked influence of certain other basic substances on the bromination of acetic anhydride have been referred to in Part II (this vol., p. 2458). The author finds that the reaction of bromine with acetone can be arrested in a similar manner. When bromine is added to acetone in carbon tetrachloride at 25°, no measurable reaction occurs for a short time; the disappearance of bromine then becomes perceptible, and almost immediately attains great speed, owing to the very powerful catalytic effect (Meyer, *Annalen*, 1911, **380**, 238) of hydrogen bromide upon enolisation in non-ionising solvents. Addition of a trace of quinoline arrests the reaction during a long period, and it seems simplest to suggest that the arrest is due to removal of hydrogen bromide as the hydrobromide (or hydrobromide perbromide, Grimaux, *Bull. Soc. chim.*, 1882, **38**, 124; Trowbridge, *J. Amer. Chem. Soc.*, 1899, **21**, 66) of the base. The well-known inhibition, by certain nitrogen-containing compounds, of gaseous photochemical reactions has been interpreted in terms of the energetics of the system (Chapman and MacMahon, J., 1909, **95**, 1718; 1910, **97**, 847) and of surface phenomena (Norrish, J., 1925, **127**, 2319), but the view here put forward of the influence of quinoline on a reaction which takes place in the liquid phase and in the dark appears to account for the observed facts.

A similar interpretation may be applied to the case of acetic anhydride, and is rendered the more probable by the fact that quinoline is without effect in presence of 1·6 equivalents of sulphuric acid. The reaction of the base with the halogen acid produced in the bromination of the enolised anhydride will prevent the formation of any appreciable quantity of acetyl bromide (or any acetyl bromide

formed may be converted into an additive compound with quinoline; Dehn, *J. Amer. Chem. Soc.*, 1912, **34**, 1408); the main series of reactions, involving the bromination of the acid bromide, is thus eliminated until sufficient hydrogen bromide has been formed (in the slow change through the enolised anhydride) to react with the whole of the base. Moreover, removal by the quinoline of the greater part of the hydrogen bromide normally present in the equilibrium $(CH_3{\cdot}CO)_2O + HBr \rightleftharpoons CH_3{\cdot}CO_2H + CH_3{\cdot}COBr$ (Part II, p. 2459) renders the enolisation of the anhydride so slow as to be imperceptible; the values of k' given in Part II refer to the rate of enolisation in presence of this hydrogen bromide. The prolonged period of inertness is thus explained. The shorter duration of this period in presence of pyridine, *iso*quinoline, triethylamine, or dimethylaniline may be attributed to a larger amount of hydrogen bromide present in equilibrium with the base and its hydrobromide, $B,HBr \rightleftharpoons B + HBr$. The relatively feeble effect of aliphatic primary and secondary amines is to be expected, since they can be acetylated by the anhydride, as is also the complete inactivity (and even slight accelerating influence) of aniline and monomethylaniline, which are not only acetylated, but also substituted in the benzene nucleus, hydrogen bromide being evolved.

The effect of acetyl nitrate (Part II) also may be ascribed to the removal of hydrogen bromide (and perhaps of acetyl bromide), with consequent elimination of the main series of reactions and the rendering of the enolisation of the anhydride imperceptibly slow. That the removal is here due to oxidation is indicated by a considerable liberation of bromine when acetyl bromide is added to acetic anhydride containing nitric acid. Addition of 4 mols. of acetyl bromide per mol. of nitric acid completely annuls the effect of the latter, while on further addition of the acid bromide the disappearance of bromine is accelerated in the normal manner. Acetyl nitrate also retards the bromination of acetone, but does not arrest the reaction completely, as quinoline does. Nitric acid, on the other hand, shortens the time needed for the reaction to become perceptible (compare Lapworth, J., 1904, **85**, 31).

The arrests referred to in Part II may be attributed, in general, therefore, to the removal of hydrogen bromide (and perhaps sometimes of acetyl bromide) as a consequence of either the basic or the oxidising quality of the inhibitor.

EXPERIMENTAL.

Bromination of Acetone in Carbon Tetrachloride.—The carbon tetrachloride was shaken with aqueous sodium hydroxide and then with water, dried, and fractionated. Acetone, purified by the

sodium iodide method, was dried over calcium chloride and fractionated. The quinoline was dried over solid potassium hydroxide and fractionated, and the nitric acid was distilled from sulphuric acid and freed from nitrous acid by passage of carbon dioxide. The velocity determinations were carried out by withdrawal at intervals of 2 c.c. of the reaction mixture, addition to aqueous potassium iodide, and titration of the iodine. In Table I, titres are expressed as c.c. of $N/50$-thiosulphate.

TABLE I.

Acetone = 0·218*M*.		Acetone = 0·109*M*.		Acetone = 0·218*M*.	
Time (mins.).	Titre.	Time (mins.).	Titre.	HNO_3 = 0·025*M*.	
0	14·48	0	13·98	Ac_2O = 0·030*M*.	
9	14·48	10	13·92	Time (hrs.).	Titre.
10	14·42	12	13·88	0	12·48
10·5	14·32	13	13·85	1	12·32
11	13·98	14	13·60	7·5	11·62
11·5	0	15	0	22·5	10·05
				31	9·32
Acetone = 0·218*M*.		Acetone = 0·218*M*.		46	8·05
HNO_3 = 0·025*M*.		Quinoline = 0·003*M*.		70	5·95
Time (mins.).	Titre.	Time (hrs.).	Titre.	119	3·75
0	12·48	0	12·58	166	1·62
5	12·48	164	12·55		
7	0	222	12·45		
		232	0		

Bromination of Acetic Anhydride.—Purification of materials and experimental procedure were as described in Part II. Titres in Table II are expressed as c.c. of $N/10$-thiosulphate. Reactions I(d) and II(b) are identical with the reaction of bromine with pure acetic anhydride.

TABLE II.

I. Effect of quinoline and sulphuric acid in conjunction; quinoline = 0·0064*M*.

	Ratio, $\frac{1}{2}H_2SO_4/C_9H_7N$.	Initial titre.	Fall in titre after (mins.) 10.	20.	30.	40.	50.	60.
(a)	1·01	10·35	0	0	0	0	0	0
(b)	1·27	10·15	0	0	0·02	0·60	1·55	3·00
(c)	1·48	9·95	0·05	0·60	1·88	3·30	4·60	5·85
(d)	1·62	10·22	0·20	1·58	2·92	4·38	5·75	7·08
(e)	1·82	10·52	0·82	2·20	3·82	5·45	6·75	8·10

II. Effect of nitric acid and acetyl bromide in conjunction; HNO_3 = 0·0032*M*.

	Ratio, AcBr/HNO_3.	Initial titre.	Fall in titre after (mins.) 15.	30.	45.	60.	75.	90.
(a)	2·0	10·75	0	0	0	0	0	0
(b)	4·3	10·70	0·72	2·55	4·68	6·72	8·18	9·10
(c)	7·3	11·15	0·75	4·10	6·60	8·22	9·32	9·95
(d)	13·4	10·75	2·32	5·30	7·30	8·68	9·60	—

In conclusion, the author wishes to express his thanks to Professor K. J. P. Orton, F.R.S., for much helpful advice and criticism, to Dr. H. I. Hughes for carrying out some of the experiments, and to the Chemical Society for a grant towards the expenses of the research.

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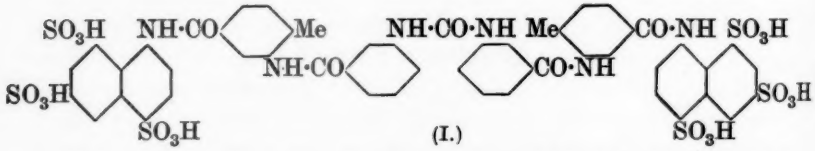
BANGOR. [*Received, October 26th*, 1927.]

CCCCVII.—*Trypanocidal Action and Chemical Constitution. Part VII.* s-*Carbamides and Arylamides of Naphthylamine-di- and -tri-sulphonic Acids with Some Observations on the Mesomorphic State.*

By ISIDORE ELKANAH BALABAN and HAROLD KING.

THE discovery of the substance known as Bayer 205 marks an epoch both in the development of chemotherapy and in the treatment of trypanosomiasis. The chemical identity of this substance remained for long undivulged owing to war conditions, but the group of substances of which it is a member was plainly covered by a series of patents taken out by the firm of Bayer from 1914 onwards (D.R.-P. 278122, etc.). The structure was elucidated by Fourneau, Tréfouel, and Vallée (*Ann. Inst. Pasteur*, 1924, **38**, 81), who showed that Bayer 205 was in all probability the *s*-carbamide of *m'*-aminobenzoyl-*m*-aminotoluoyl-1-naphthylamine-4 : 6 : 8-trisulphonic acid (I).



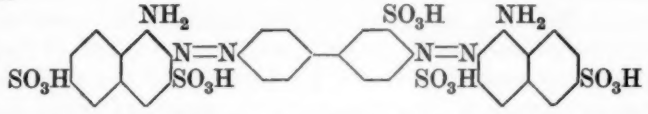
(I.)

It is natural that the discovery of an intensely trypanocidal agent like Bayer 205, colourless and containing no metallic group to which its toxic properties might be referred, should stimulate enquiry into the general principles governing its mode of action. On this point the patents are not informative, but Heymann (*Z. angew. Chem.*, 1924, **37**, 585) and Röhl (*Arch. Schiff. Trop. Hyg.*, 1926, **30**, *Beiheft* **1**, 103), both of the firm of Bayer and representing respectively the chemical and the pharmacological side, have contributed considerably to an insight into the general principles involved.

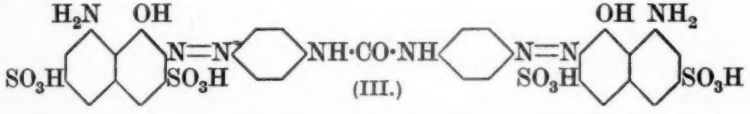
As early as 1904 Ehrlich and Shiga made the fundamental dis-

covery that Trypan-red (II), a member of the Congo-red series of cotton dyes, can cure an experimental infection of trypanosomiasis in mice.

(II.)



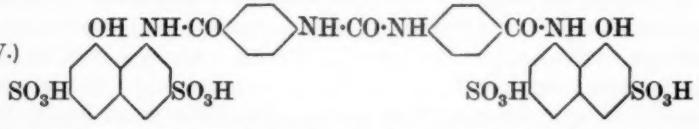
Following on this, Nicolle and Mesnil, in a classic paper (*Ann. Inst. Pasteur*, 1906, **20**, 417), examined a long range of cotton dyes all belonging to the Congo-red type and found the substance having the best curative action on infection with *Trypanosoma gambiense* in rats and monkeys to be the *s*-carbamide (III), a derivative of 1 : 8-aminonaphthol-3 : 6-disulphonic acid (H-acid) called Afridol Violet.



(III.)

There are obvious disadvantages in dyes as therapeutic agents when applied to man or cattle, and if the therapeutic action of dyes is due to fixation by tissues it should be possible to prepare colourless substances of similar build and similar properties. The chemists of the firm of Bayer therefore chose as their starting point H-acid and prepared (IV), the colourless analogue of (III).

(IV.)



This substance delayed the death of mice suffering from trypanosomiasis by one day. Now from contemporaneous work on *dyes* it was known that substantive character to cotton was favoured by the presence of chains of aminobenzoyl groups and by the linking of these by carbonyl chloride. When, therefore, the aminobenzoyl groups in (IV) were duplicated in chain formation there was an increase of activity, but a falling off when they were triplicated. By chemical evolution from this striking discovery there resulted the gradual elaboration of the substance Bayer 205. It is quite clear from Heymann's account that the discovery of Bayer 205 arose from the recognition of the fact that it is possible to prepare colourless substances of substantive properties, which, being of similar molecular build to trypanocidally active dyes, also exhibit trypanocidal properties.

Röhl (*loc. cit.*), while also recognising the substantive properties

of these colourless substances, made the significant observation that these colourless complex carbamides form precipitates at very high dilutions with some of the simplest basic proteins, *e.g.*, clupeine, salmine, thymine, and sturine—constituents of the spermatozoa of fish. As a consequence, he supposes that the action of Bayer 205 on trypanosomes is due to a combination of the sulphonic acid groups with basic cell constituents of the parasites forming difficultly soluble salts.

Although the outline of a plausible picture of the principles underlying the action of Bayer 205 has been presented, no experimental evidence has been adduced in support of it. The work detailed in this communication was therefore undertaken in order to familiarise ourselves with this important field and to test the views which have been advanced.

For this purpose six readily accessible naphthylaminedisulphonic acids have been used as a starting point, *viz.*, Freund's acid (1-naphthylamine-3 : 6-disulphonic acid), amino-G-acid (2-naphthylamine-6 : 8-disulphonic acid), C-acid (2-naphthylamine-4 : 8-disulphonic acid), amino-J-acid (2-naphthylamine-5 : 7-disulphonic acid), H-acid (8-hydroxy-1-naphthylamine-3 : 6-disulphonic acid), and 2R-acid (8-hydroxy-2-naphthylamine-3 : 6-disulphonic acid).

These with the exception of H-acid have been converted into their *s*-carbamides, H-acid under the same conditions yielding the internal *ON*-carbonyl derivative, 1 : 8-ON-*carbonylaminonaphthol*-3 : 6-*disulphonic acid*. They have also been converted into their *m*-nitrobenzoyl derivatives and these in turn into the *m*-aminobenzoyl derivatives. The latter have been phosgenated to form the *s*-carbamides and have also been converted into the *m'*-nitrobenzoyl-*m*-aminobenzoyl derivatives. The latter have finally been reduced to the *m'*-aminobenzoyl-*m*-aminobenzoyl derivatives, which on phosgenation have given the *s*-carbamides. The general scheme of synthesis is shown below :

$$\begin{array}{rl} \downarrow & \\ & NH_2R \longrightarrow RNH{\cdot}CO{\cdot}NHR \\ & NO_2{\cdot}Bz{\cdot}NHR \quad (\textit{First carbamide}) \\ & (1st)\ NH_2{\cdot}Bz{\cdot}NHR \longrightarrow RNH{\cdot}Bz{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}Bz{\cdot}NHR \\ \downarrow & NO_2{\cdot}Bz{\cdot}NH{\cdot}Bz{\cdot}NHR \quad (\textit{Second carbamide}) \\ & (2nd)\ NH_2{\cdot}Bz{\cdot}NHBz{\cdot}NHR \longrightarrow RNH{\cdot}BzNH{\cdot}BzNH{\cdot}CO{\cdot}NHBz{\cdot}NHBz{\cdot}NHR \\ & \qquad\qquad\qquad\qquad\qquad\qquad (\textit{Third carbamide}) \end{array}$$

$$(Bz = {\cdot}C_6H_4{\cdot}CO{\cdot})$$

These have all been isolated in a state of purity free from sodium chloride and, excluding the nitro-compounds, have been tested for toxicity on normal mice and for trypanocidal action on mice infected experimentally with *T. equiperdum*. The maximum doses

tolerated by mice expressed in milligrams per gram of mouse are given in the following table :

	Aminobenzoyl derivatives.		Carbamides.		
	First.	Second.	First.	Second.	Third.
Freund's Acid	4·0	3·25	>2·0	1·5	0·4
Amino-G-Acid	1·5	1·0	1·75	**0·5**	**0·2**
C-Acid	3·0	1·0	2·0	**1·0**	**0·3**
Amino-J-Acid	3·0	0·75	1·75	**1·0**	0·3
H-Acid	2·25	1·0	3·0 *	**0·3**	**0·3**
2R-Acid	>2·5	0·7	2·0	0·1	0·2

* *ON*-Carbonyl derivative.

It will be observed that there is a very rough parallelism between the corresponding derivatives of different acids. The only compounds showing any trypanocidal action, and that of a low order as indicated below, are those carbamides the tolerated doses of which are expressed in heavy type. For these, the curative action is shown in the following table, each substance as a rule being tested on 4 or 5 infected mice, and r signifying the number of days before relapse occurred in the most favourable cases :

	Second carbamide.	Third carbamide.
Amino-G-Acid	0·3, $r = 4$	0·2, $r = 7$
C-Acid	0·5, $r = 5$	0·3, $r = 12$
Amino-J-Acid	0·5, $r = 1$	No action
H-Acid	0·2, $r = 5$	0·175, $r = 5$

The striking fact emerges from these results that trypanocidal activity only appears at the *s*-carbamide stage of combination of the aminobenzoyl and aminobenzoylaminobenzoyl derivatives and that there is no trace of activity in any of the aminobenzoyl compounds. All the derivatives, moreover, of Freund's acid and of 2R-acid examined were inactive. This is contrary to the claim made in D.R.-P. 288273, where the *s*-carbamide of *m'*-aminobenzoyl-*m*-aminobenzoyl-1-naphthylamine-3 : 6-disulphonic acid is said to cause the disappearance of trypanosomes from the blood of infected animals at high dilutions. This particular substance had not the slightest detectable action on the course of infection of *T. equiperdum* in mice, and trypanosomes exposed to 1% concentration of it for 24 hours *in vitro* were not rendered non-infective by it.

As the efficacy of the above-mentioned active carbamides was of a very low order, it was deemed of interest to investigate the corresponding series of compounds from the parent 1-naphthylamine-4 : 6 : 8-trisulphonic acid * contained in Bayer 205, particularly as Fourneau *et alii* (*loc. cit.*) have recorded a chemotherapeutic index, C/T, of 1/12 for the *s*-carbamide of *m'*-aminobenzoyl-

* For brevity of nomenclature, this acid is hereinafter referred to as B-Acid, following Fourneau (*loc. cit.*).

m-aminobenzoyl-1-naphthylamine-4 : 6 : 8-trisulphonic acid, and Röhl (*loc. cit.*) states that the simple *s*-carbamide of B-acid is weakly active.

The following table gives the tolerated and the curative doses observed for the parallel series of derivatives of B-acid.

		Aminobenzoyl derivatives.		Carbamides.		
	Acid.	First.	Second.	First.	Second.	Third.
Dosis tolerata ...	3·0	2·0	1·5	>4·0	1·0	0·3
Dosis curativa ...	None	None	None	4·0, $r > 30$ 2·5, $r = 15$	None	0·15, $r > 30$

This table supports the main conclusion drawn from the previous tables that trypanocidal activity is only found in the *s*-carbamides and is absent from the parent acids and their aminobenzoylated derivatives.

Substantive Properties and Trypanocidal Action.

Although the recognition of the substantivity of colourless substances, *i.e.*, their affinity for natural fibres, was in the minds of the discoverers of Bayer 205 and led to its development, the question arises whether the therapeutic action of Bayer 205 or any of its analogues is due to this substantive property. Fortunately, this can, at least to some extent, be submitted to the test of experiment.

As the result of preliminary trials on the dyeing at 100° of pure wool, silk, and cotton by two members of the Congo-red series of dyes, namely, Trypan-red and Trypan-blue, with and without the use of "assistants," it was found that cotton was the most suitable fibre and sodium chloride the best "assistant." The same conditions could now be applied to the invisible dyeing of cotton by the colourless series of substances synthesised and tested for trypanocidal activity as related above. A limitation is, however, imposed in that it is only possible to "develop" the invisibly dyed cotton in those instances where there is a free naphthol group present. This limits the applicability of this mode of detection of the degree of substantivity of these colourless substances to the derivatives of H-acid and 2R-acid. Accordingly each substance (0·01 g.) mentioned in the table below was dissolved in water (10 c.c.), sodium chloride (0·5 g.) added, and a cotton skein (0·5 g.) immersed in the solution. The solution was heated at 100° for 1½ hours; the cotton was then removed and washed five times by decantation with water, 50 c.c. each time, and the colour was developed on the cotton by immersion in neutral diazotised *p*-nitroaniline at 12° as recommended for developing colour on cotton in

dyeing practice. After thorough washing, the skeins of cotton were dried, and the colour intensities compared by means of a Lovibond tintometer. The same conditions were used with derivatives of 2R-acid except that 2·5% sodium chloride was used, higher concentrations having a salting-out effect even at 100°. The following table gives the relative colour intensities of the dyed skeins of cotton expressed in terms of the content of naphthol, the assumption being made that the azo-compounds formed from a given acid and its derivatives are all analogously constituted and of equal tinctorial value per unit naphthol molecule. The free acids, their first carbamides, and their first nitrobenzoyl derivatives are omitted from the table, as they were under these conditions devoid of substantive property.

	Aminobenzoyl derivatives.		Nitrobenzoyl derivatives.	Carbamides.	
	First.	Second.	Second.	Second.	Third.
H-Acid	1	2	1	4	6
2R-Acid	4	5	2	9	12

The salient feature of this table is the pronounced maximum of substantivity to cotton at the *s*-carbamide stage of combination exhibited by these colourless substances, which are built up on the type or model of the Congo-red series of cotton dyes. Now it is precisely at the *s*-carbamide stage of combination that trypanocidal activity appears, so that there seems to be a parallelism between the substantive property of these carbamides to cotton and their trypanocidal activity. When the same conditions were applied to wool there was no selective substantivity exhibited.

In further support of this parallelism, it has been shown that the most active of all trypanocidal agents, Bayer 205, is also substantive to cotton. This cannot be demonstrated by development on the fibre, since Bayer 205 will not couple with diazotised amines, but it can be effected by making use of the observations of Röhl that these complex carbamides form precipitates with some of the simplest basic proteins at high dilutions. For this purpose, clupeine sulphate was chosen, as it is readily obtained from herrings' roe. The sensitiveness of the test for the detection of Bayer 205 by clupeine sulphate is not very great, but it may be increased by addition of 20% sodium chloride solution, as is shown in the following table :

Dilutions of Bayer 205	1 in 5,000	1 in 10,000	1 in 50,000	1 in 100,000
1 C.c. + 2 drops 1% clupeine sulphate	Ppt.	Turbid	Clear	Clear
Bayer 205 + 20% NaCl	1 in 5,000	1 in 10,000	1 in 50,000	1 in 100,000
1 C.c. + 2 drops clupeine sulphate...	Ppt.	Ppt.	Turbid	Faint turbidity

Higher concentrations of sodium chloride have a salting-out effect on the clupeine sulphate.

The absorption of Bayer 205 by cotton was investigated by means of this reaction in the following way: Skeins of cotton (0·1 g.) were extracted in succession with pure ether, absolute alcohol, and several changes of boiling water and then dried. They were added to a solution of Bayer 205 (1·5 c.c.) containing sodium chloride (0·3 g.) and heated at 100° in stoppered tubes for an hour. When cool, 1 c.c. was removed and treated with 2 drops of 1% clupeine sulphate. The results of a series of experiments with controls are in the following table:

Tube.	Contents.	Reagent 2 drops clupeine sulphate.
1	1·5 c.c. of 1 in 50,000 Bayer 205 + 0·3 g. NaCl + 0·1 g. cotton.	Solution clear.
2		
3	1·5 c.c. of 1 in 50,000 Bayer 205 + 0·3 g. NaCl.	Standard turbidity for this dilution.
4		
5	1·5 c.c. of water + 0·1 g. cotton + 0·3 g. NaCl.	Solution clear.
6		

It therefore follows that Bayer 205 at a dilution of 1 in 50,000 is removed by cotton in the presence of sodium chloride, the concentration of Bayer 205 falling below 1 in 100,000. It would be of great interest to apply this method of detecting the substantive property to cotton of these colourless substances to the trypanocidally active series of B-acid described above. Unfortunately, it is extremely difficult, especially with limited supplies of material, to free them from sodium chloride, the uncontrolled presence of which would interfere seriously with the tests.

It was naturally of interest to determine whether the variation of the substantive property with structure was paralleled by the insolubility of the complexes formed between the protamines and the sulphonic acids. For this purpose, the *m*-aminobenzoyl and *m'*-aminobenzoyl-*m*-aminobenzoyl derivatives of H-acid and 2R-acid and the corresponding *s*-carbamides were compared in respect of their precipitability at high dilutions by clupeine sulphate. It was found that the *s*-carbamides did not form complexes of outstanding insolubility, but rather that they were very slightly more soluble than the complexes with the corresponding amines.

It may therefore be suggested on the basis of the limited number of examples examined by us that there appears to be a rough parallelism between the substantivity to cotton and trypanocidal action *in vivo*, in that salient peaks of substantivity occur at the *s*-carbamide stage of combination and trypanocidal action is only found in the *s*-carbamides. The interpretation of this is probably that substantivity to cotton is paralleled by the substantivity either

to the tissues of the mammalian host or to the trypanosomes or to both.

The Mesomorphic State of Derivatives of Naphthylaminedisulphonic Acids.

The recognition of the mesomorphic or liquid crystalline state of matter is largely due to the pioneering labours from 1877 onwards of O. Lehmann. The development of the subject has been mainly confined to pure crystalline substances which when melted showed anisotropy or which, when converted into the isotropic liquid state by heat, developed the anisotropic fluid phase on cooling. This field has been especially enriched by Vörlander's syntheses of numerous organic compounds showing this property. Within the last few years an extension of the subject has taken place in that it has been shown that anisotropic fluids may separate from aqueous media and the richest field in this respect is that of the soaps.

It is historically of interest that the first anisotropic fluid ever observed belonged to the latter class. Virchow in 1854 (*Arch. path. Anat. Physiol.*, **6**, 562) showed that the material separating from a hot alcoholic extract of brain tissue or spinal cord in contact with water swelled up with production of the so-called "myelin-forms" and in 1858 Mettenheimer made the important observation that the "myelin-forms" were anisotropic. There is little doubt that it is the combined fatty acids present in the phosphatides (lecithin, cephalin, phrenosin, etc.) which are primarily responsible for this property. In 1866, Neubauer (*ibid.*, **36**, 303) obtained "myelin-forms" by exposure of oleic acid to ammonia, but Lehmann first recognised the crystalline fluid phase of the oleic acid salts (*Ann. Physik*, 1895, **56**, 771). During subsequent years there are occasional references to be found to the anisotropy of soap solutions or to the anisotropy of "myelin-forms" produced from soaps (Krafft, *Z. physiol. Chem.*, 1902, **35**, 364, 376; Adami and Aschoff, *Proc. Roy. Soc.*, 1906, **78**, *B*, 30; Friedel, *Ann. Physique*, 1922, **18**, 273). In 1923, however, Maclennan (*J. Soc. Chem. Ind.*, **42**, 393) revealed the rich field of anisotropic fluids from aqueous solutions covered by the soaps and following on this McBain and Langdon (J., 1925, **127**, 852) and McBain and Elford (J., 1926, 421) have given a full account of the set of equilibria which govern such systems.

The compounds described in this paper are rich in examples of anisotropic fluids from aqueous media and provide a wonderful wealth of material for quantitative study. So far they have only been examined qualitatively, and incidentally to the main theme of this communication, but the qualitative observations lead one

to believe that the whole group of phenomena are subject to the limitations imposed by the phase rule. Structurally the compounds exhibiting this property are far removed from the fatty-acid type and are more akin to the isolated cases of mesomorphy of 10-bromo- and 10-chloro-phenanthrene-3(or 6)-sulphonic acid of Sandqvist (*Ber.*, 1915, **48**, 2054; *Kolloid Z.*, 1916, **19**, 113; *Arkiv Kemi*, 1916, **7**, No. 2).

Of the compounds described in this paper, the phenomenon of mesomorphy is restricted to those derived from disulphonic acids of the naphthylamines and has been observed in derivatives of each of the disulphonic acids mentioned on p. 3070, but is particularly pronounced in derivatives of C-acid, amino-J-acid, and amino-G-acid. Among these derivatives, it may occur as early as the first *m*-nitrobenzoyl derivative and be found in all the subsequent derivatives up to the *s*-carbamide of the *m'*-aminobenzoyl-*m*-aminobenzoyl derivative. As a rule it seems to be the least pronounced in the *s*-carbamides.

Derivatives of the naphthylaminedisulphonic acids show a general resemblance in behaviour. They are soluble in hot water and on being allowed to cool usually give, not crystals which are amenable to filtration, but, rather, highly hydrated products which vary greatly in consistency; they may be waxy solids, limpid fluids possessed of a sheen, clear gels or worm-like growths, and are in almost all cases strongly birefringent. The high degree of hydration seems essential for their production, for, if allowed to form from 50% or higher strengths of alcohol, they usually separate in the solid crystalline state, a totally distinct phase amenable to filtration and processes of washing. It is only in this manner in many cases that it is possible to obtain the products pure and free from inorganic salts. As a rule, the products are readily salted out from aqueous solutions by sodium chloride in a caseous form which lends itself to filtration. It has not been possible to decide whether this caseous phase is a new phase, in the same sense that the curds obtained in the soap-boiling process are a new phase giving an *X*-ray pattern, unobtainable from the anisotropic fluid phase of soaps, or is merely a stage in the dehydration of the anisotropic fluids. Such qualitative evidence as we possess suggests that under the dehydrating action of sodium chloride or alcohol it is possible to pass gradually from a limpid anisotropic fluid in equilibrium with its saturated isotropic solution to the caseous form in equilibrium with a concentrated solution of sodium chloride or alcohol. The intermediate anisotropic fluid appears to possess a certain degree of rigidity, but always flows under pressure of a cover-slip. In many cases, the caseous form passes with lapse of

time into the crystalline solid phase, probably with some change in the degree of hydration. It follows from what has been said about the hydration of the anisotropic fluid phase that, if the pure solid crystalline form be redissolved in the minimum volume of boiling water, then, on cooling, the anisotropic fluid phase may separate and, owing to its high degree of hydration, may combine with the whole of the water present, giving a single anisotropic fluid phase. Such we believe we have observed in the case of the monosodium salt of *m*-aminobenzoyl-2-naphthylamine-5 : 7-disulphonic acid (see Experimental). In other cases, a biphasic fluid may result from equilibrium of the anisotropic fluid with its isotropic saturated aqueous solution. The stability of such solutions varies. The specific instance quoted above lends itself particularly to demonstration purposes, as the viscous anisotropic fluid may persist at room temperature for months and then pass into a sparingly soluble, microscopically fine crystalline solid in equilibrium with a limpid saturated solution. To the naked eye both conditions of the solution possess a sheen and are indistinguishable. In the case of the tetrasodium salt of the *s*-carbamide of *m'*-aminobenzoyl-*m*-aminobenzoyl-2-naphthylamine-6 : 8-disulphonic acid, it has been possible to observe, by means of the polarising microscope, the slow crystallisation of the solid phase at the expense of the surrounding anisotropic fluid. In other cases, the anisotropic fluid phase appears to be permanently stable, as samples have been kept for 2 years.

The converse phenomenon, formation of the anisotropic fluid phase at the expense of the crystalline solid phase, has been observed in the case of the disodium salt of *m'*-nitrobenzoyl-*m*-aminobenzoyl-2-naphthylamine-6 : 8 -disulphonic acid and in the case of the free acid, *m'*-nitrobenzoyl-*m*-aminobenzoyl-2-naphthylamine-4 : 8-disulphonic acid (see Experimental).

In appearance the anisotropic fluids, whether in presence of and in equilibrium with their saturated isotropic aqueous solutions or not, usually possess a sheen, and examined under the highest power of the microscope are never particulate. Under the polarising microscope they present alternations of dark and light patches and under pressure of a cover-slip show streaming of the light patches. The densities of the anisotropic fluid phase and the isotropic fluid phase in equilibrium are usually very close, as there is no evidence of settling, but on prolonged centrifuging a partial separation may be effected, the supernatant phase being clear and isotropic and the lower portion now exhibiting an orientation of the sheen in spiral form. The production of a sheen is by no means invariable, and cases are described in the experimental portion of clear anisotropic gels and of clear anisotropic viscous solutions.

The mimicry of crystalline form by liquid crystals has often been observed (Lehmann, Vörlander) and a good instance of such in aqueous media is presented by the sodium hydrogen salt of *m'*-aminobenzoyl-*m*-aminobenzoyl-2-naphthylamine-4 : 8-disulphonic acid.

The derivatives of 1-naphthylamine-4 : 6 : 8-trisulphonic acid, on the other hand, show none of these phenomena and as a rule are extremely soluble in water and salted out with difficulty. The following table shows the incidence of this property :

Salted out.	Not salted out.
RNH_2	$(RNH)_2CO$
NO_2·Bz·NHR	NH_2·Bz·NHR
NO_2·Bz·NH·Bz·NHR	$(RNH·Bz·NH)_2CO$
NH_2·Bz·NH·Bz·NHR (diNa salt)	NH_2·Bz·NH·Bz·NHR (triNa salt)
	$(RNH·Bz·NH·Bz·NH)_2CO$

It is of interest that the substance Bayer 205 (I), which only differs from the last member here tabulated by two methyl groups, is extremely soluble in water and is also not salted out. It occurs commercially as a white powder devoid of crystalline structure, but according to our own observations it may readily be crystallised by solution in a fraction of its weight of water, addition of several volumes of pure methyl alcohol, followed by gradual addition of acetone. It separates after some delay in clusters of needles.

It is a pleasure to recognise our indebtedness to the following: to Miss Durham and Miss Marchal of this Department for carrying out the many biological experiments; to Dr. A. Schedler of the Clayton Aniline Co. for gifts of pure wool, silk, and cotton; to Dr. J. T. Conroy of the United Alkali Co. for a free and liberal supply of carbonyl chloride, and to the Pharmazeutische Abteilung of the I.G. Farbenindustrie Aktiengesellschaft for a gift of 1-naphthylamine-4 : 6 : 8-trisulphonic acid.

Experimental.

m-*Nitrobenzoyl*-1-*naphthylamine*-3 : 6-*disulphonic Acid*.—1-Naphthylamine-3 : 6-disulphonic acid (Freund's acid, 12·1 g.) was dissolved in 40 c.c. of *N*-sodium hydroxide (1 mol.) and 20 c.c. of water and treated with 14·85 g. (2 mols.) of *m*-nitrobenzoyl chloride, all at once, and the mixture was shaken for ½ hour with addition of a few drops of ether. Three successive portions (each 40 c.c.) of *N*-sodium hydroxide were then added at half-hourly intervals with subsequent shaking. The solution was made distinctly acid to Congo-paper, the *m*-nitrobenzoic acid removed by ether, the aqueous liquor neutralised to litmus and concentrated under reduced pressure at 50°, and two crops of the *disodium* salt collected (yield, 75%). This salt is readily soluble in water (1 in 26) and is precipitated in microscopic, triangular leaflets on addition of sodium chloride.

For analysis it was crystallised from 50% alcohol (Found : Loss at 140°, 16·3. $C_{17}H_{10}O_9N_2S_2Na_2,5\frac{1}{2}H_2O$ requires H_2O, 16·6%. Found in dried salt : Na, 9·1. $C_{17}H_{10}O_9N_2S_2Na_2$ requires Na, 9·3%). An aqueous solution of the salt is neutral to litmus and gives crystalline precipitates on addition of calcium, magnesium, and barium chlorides. The salt will also crystallise unchanged from solutions which are acid to Congo-paper.

m-*Aminobenzoyl*-1-*naphthylamine*-3 : 6-*disulphonic Acid*.—To a solution of 25 g. of the crude sodium salt (above described) in 195 c.c. of 2*N*-sodium hydroxide at 0°, ferrous chloride (70 g.; 7 mols.) in 100 c.c. of water was added slowly with stirring, followed by 195 c.c. of 2*N*-sodium hydroxide to make the solution definitely alkaline. After filtration the ferric hydroxide sludge was extracted twice with 250 c.c. of 0·2*N*-sodium hydroxide each time and the solution was neutralised and concentrated at 50°; the sparingly soluble azoxy-compound (1·7 g.) separated first, followed by the *disodium* salt (13·5 g.) of the required amino-acid. This crystallises from water, in which it is very readily soluble, in fine needles (Found : Loss at 160°, 16·6. $C_{17}H_{12}O_7N_2S_2Na_2,5H_2O$ requires H_2O, 16·2%. Found in anhydrous salt : Na, 9·5. $C_{17}H_{12}O_7N_2S_2Na_2$ requires Na, 9·9%). It gives a moderately easily soluble *diazo*-compound free from chloride but containing sodium, as a primrose-yellow precipitate of needles. This couples with glyoxaline derivatives in aqueous sodium carbonate, the solutions having a cherry-red colour. The disodium salt in concentrated solution gives a *calcium* salt, microscopic prisms, and a *barium* salt, sheaves of flat prisms, on addition of saturated calcium or barium chloride. The *silver* salt separates similarly as a microcrystalline powder.

The *sodium hydrogen* salt is much less soluble than the disodium salt and rapidly separated in flattened prisms when the latter (2·9 g.) in 5 c.c. of water was treated with 1 c.c. of concentrated hydrochloric acid (yield, 2·6 g.) (Found : Loss at 160°, 15·6. $C_{17}H_{13}O_7N_2S_2Na,4\frac{1}{2}H_2O$ requires H_2O, 15·4%. Found in anhydrous salt : Na, 5·1. $C_{17}H_{13}O_7N_2S_2Na$ requires Na, 5·2%).

The *azoxy-compound* is readily soluble in 8 parts of hot water and crystallises in yellow, silky, hair-like needles (Found : Loss at 95°, 18·5. $C_{34}H_{20}O_{15}N_4S_4Na_4,12H_2O$ requires H_2O, 18·6%. Found in anhydrous salt : Na, 9·2. $C_{34}H_{20}O_{15}N_4S_4Na_4$ requires Na, 9·7%).

m′-*Nitrobenzoyl*-m-*aminobenzoyl*-1-*naphthylamine*-3 : 6-*disulphonic Acid*.—The disodium salt of the preceding acid (10·7 g., 87% anhydrous salt) dissolved in 50 c.c. of water was nitrobenzoylated with two equivalents of acid chloride as described in the first stage of the synthesis. The final solution was made distinctly acid to

Congo-paper and the gelatinous precipitate was collected and dissolved in water. The two solutions were then thoroughly extracted with ether, combined, neutralised, and concentrated at 50°, and the successive crops of gelatinous nitro-acid collected. These were dissolved in boiling water and treated with 10 volumes of alcohol and the solution was kept until the gelatinous nitro-compound which first separated had changed into a crystalline mass of soft, white needles (yield, 11 g.) (Found in product from 90% alcohol: Loss at 160°, 11·0. $C_{24}H_{15}O_{10}N_3S_2Na_2,4H_2O$ requires H_2O, 10·5%. Found in anhydrous salt: Na, 7·6. $C_{24}H_{15}O_{10}N_3S_2Na_2$ requires Na, 7·5%). This *nitro-amide* is readily soluble in water with a neutral reaction and couples only faintly with Pauly's reagent in sodium carbonate solution. It is fairly readily soluble in boiling methyl alcohol, but does not crystallise well from it.

m′-*Aminobenzoyl*-m-*aminobenzoyl*-1-*naphthylamine*-3:6-*disulphonic Acid*.—The preceding nitro-acid (10·2 g.) was reduced with ferrous chloride exactly as described at a previous stage. The alkaline filtrates and extracts of the ferric hydroxide were made neutral to Congo-paper; the thick, gelatinous precipitate which first separated soon became wholly crystalline (yield, 10·1 g.). The mother-liquors on concentration only deposited a further 0·25 g. This *amino-acid* is a *monosodium* salt and is soluble in 3 volumes of boiling water, separating as a thick felt of small, silky needles on cooling (Found: Loss at 160°, 24·0. $C_{24}H_{18}O_8N_3S_2Na,10H_2O$ requires H_2O, 24·2%. Found in anhydrous salt: Na, 3·9. $C_{24}H_{18}O_8N_3S_2Na$ requires Na, 4·1%). An aqueous solution of the salt colours Congo-paper faintly blue. The salt forms a sparingly soluble *diazo*-compound, crystallising in microscopic needles, which couples with alkaline β-naphthol with the usual red colour. The diazo-compound is free from chloridion but contains sodium.

s-*Carbamide of* 1-*Naphthylamine*-3:6-*disulphonic Acid*.—Freund's acid (5 g.) in 250 c.c. of water containing 35 g. (20 mols.) of anhydrous sodium carbonate was submitted to a slow stream of carbonyl chloride until the reaction was acid to Congo-paper. The main bulk of the carbamide had separated (5·1 g.). When dissolved in 33 c.c. of boiling water and neutralised to litmus paper, it separated on cooling in long, silky needles with a faint pink colour. It gave no reaction for amino-groups and was free from chloride (Found: Loss at 160°, 25·6. $C_{21}H_{12}O_{13}N_2S_4Na_4,14H_2O$ requires H_2O, 25·9%. Found in anhydrous salt: Na, 12·6. $C_{21}H_{12}O_{13}N_2S_4Na_4$ requires Na, 12·8%). This *carbamide* is soluble in cold water to the extent of 8%, but is very readily salted out by sodium chloride.

s-*Carbamide of* m-*Aminobenzoyl*-1-*naphthylamine*-3:6-*disulphonic Acid*.—Five g. of the *m*-aminobenzoyl amide were phosgenated as

described in the foregoing section. The solid which had separated was collected, dissolved in 50 c.c. of hot water, and inoculated with the needle form of the carbamide. The required carbamide then separated in balls of long, silky needles (yield, 3·75 g.). This *carbamide* separates from concentrated aqueous solutions in gelatinous, rounded masses which are optically anisotropic, showing black crosses under the polarising microscope. On keeping in more dilute solution, they become transformed into the needle form. It is also readily salted out in gelatinous, anisotropic masses (Found: Na, 7·2; loss at 160°, 21·7. $C_{35}H_{22}O_{15}N_4S_4Na_4,14\frac{1}{2}H_2O$ requires Na, 7·5; H_2O, 21·4%).

s-*Carbamide of* m′-*Aminobenzoyl*-m-*aminobenzoyl*-1-*naphthylamine*-3 : 6-*disulphonic Acid.*—The phosgenation was carried out in the same way as the preceding. Complete separation of the partly precipitated carbamide was effected by addition of sodium chloride. The gelatinous solid from 6 g. of amino-compound was dissolved in 30 c.c. of hot water, neutralised, and treated with 7 volumes of alcohol. On keeping, the carbamide separated in finely divided and partly anisotropic particles free from chloride. The product was again crystallised and gave 3·6 g. of carbamide (Found: Loss at 160°, 17·0; Na, 6·2. $C_{49}H_{32}O_{17}N_6S_4Na_4,14H_2O$ requires H_2O, 17·4; Na, 6·3%). This *carbamide*, so prepared, is very soluble in water and separates from concentrated solutions in voluminous, anisotropic, waxy masses. It is precipitated by strong mineral acid as a fine, amorphous precipitate, but is only salted out with difficulty and yields a sparingly soluble, amorphous *barium* salt.

m-*Nitrobenzoyl*-2-*naphthylamine*-5 : 7-*disulphonic Acid.*—Amino-J-acid (10·2 g. = 9·7 g. of anhydrous salt) in 100 c.c. of water was nitrobenzoylated as described above. After acidification, extraction with ether, and neutralisation the solution was concentrated at 50° and the successive crops were collected without washing, until sodium chloride began to separate. The crude solid was dissolved in 50 c.c. of hot water and treated with 50 c.c. of alcohol; it then gradually separated in clusters of small needles (yield, 15·2 g.) (Found: Loss at 160°, 16·9; Na, 7·4. $C_{17}H_{10}O_9N_2S_2Na_2,5\frac{1}{2}H_2O$ requires H_2O, 16·6; Na, 7·7%). This *nitro-amide* is extremely readily soluble in water, and very concentrated aqueous syrupy solutions deposit fibre- or worm-like anisotropic growths at first, but on keeping, fine needles.

m-*Aminobenzoyl*-2-*naphthylamine*-5 : 7-*disulphonic Acid.*—The nitro-amide was reduced at room temperature with ferrous chloride and alkali as described above. The combined alkaline filtrates and extracts of the ferric hydroxide on neutralisation to Congo-paper gave a copious, white, microcrystalline precipitate of the amino-

compound. The yield was practically quantitative. The solid was dissolved in the minimum volume of boiling water (about 30 volumes). When cold, the product consisted of an opaque, viscous, anisotropic fluid with elastic properties and possessed of a crystalline sheen. There was no separation into two phases on prolonged centrifuging. The liquid crystalline condition was unaltered by addition of dilute acids, but either alcohol or sodium chloride precipitated anisotropic gelatinous masses. On keeping for various periods, 5 days to 3 months, the viscous fluid passed spontaneously into a more stable condition with separation of microscopic needles in almost quantitative amount (Found: Loss at 160°, 14·4; Na, 4·6. $C_{17}H_{13}O_7N_2S_2Na,4H_2O$ requires H_2O, 14·0; Na, 4·4%). When diazotised in dilute acid solution, it yields a gelatinous *diazo-compound*. The *disodium* salt is extremely soluble in water, the solution soon becoming brown.

m'-*Nitrobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-5 : 7-*disulphonic Acid*.—The foregoing amino-compound (10·3 g.) in 170 c.c. of water was nitrobenzoylated as described for previous members. The final solution was neutral and contained the required nitro-amide in suspension as a finely-divided, crystalline solid. This was collected and the mother-liquors after removal of nitrobenzoic acid and concentration gave only a small quantity of nitro-amide. The combined solids crystallised from 150 c.c. of boiling water, with final addition of 150 c.c. of alcohol, in small, silky needles (yield, 14·0 g.) (Found: Loss at 160°, 21·1; Na, 5·6. $C_{24}H_{15}O_{10}N_3S_2Na_2,9H_2O$ requires H_2O, 20·9; Na, 5·9%). This *amide* is readily soluble in warm water and separates from the solution, on cooling, as a white, anisotropic, gelatinous mass. From very dilute solutions it separates in microscopic needles. Its aqueous solution is neutral to litmus, and sodium chloride produces an anisotropic, gelatinous precipitate.

m'-*Aminobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-5:7-*disulphonic Acid*.—The foregoing nitro-compound (7·7 g.) in 250 c.c. of water was reduced at 30—35° with ferrous chloride and alkali. The faintly alkaline mixture was stirred for 2 hours; all traces of the white, gelatinous ferrous salt had then disappeared. The filtrate and alkaline extracts of the ferric hydroxide on neutralisation to Congo-paper gave a gelatinous, anisotropic precipitate of the amino-compound. The mother-liquors gave a further small crop of 0·65 g. The product was crystallised from 125 c.c. of boiling water with addition of 125 c.c. of alcohol and gave 5·35 g. of soft balls of microscopic, silky needles of the *sodium hydrogen* salt (Found: Loss at 160°, 15·3; Na, 3·8. $C_{24}H_{18}O_8N_3S_2Na,5\frac{1}{2}H_2O$ requires H_2O, 15·0; Na, 3·5%). This sodium salt is readily soluble in boiling water, and on cooling, the solution yields a white, turbid, anisotropic

fluid with a crystalline sheen. Clear aqueous solutions give gelatinous precipitates at high dilutions with 3*N*-hydrochloric acid. It diazotises and then couples in the usual way with β-naphthol. The *disodium* salt is readily soluble in cold water and crystallises in soft, woolly needles (Found: Loss at 160°, 17·1; Na, 6·3. $C_{24}H_{17}O_8N_3S_2Na_2,6\frac{1}{2}H_2O$ requires H_2O, 16·7; Na, 6·5%).

s-*Carbamide of* 2-*Naphthylamine*-5 : 7-*disulphonic Acid*.—When this naphthylamine was phosgenated in 50 volumes of water with sodium carbonate (20 mols.), there was no separation of solid, but on saturation with sodium chloride the carbamide was precipitated in short needles. It was collected and re-phosgenated under the same conditions and again precipitated. It was dissolved in hot water, neutralised, and crystallised by addition of 3 volumes of alcohol. It was recrystallised and gave 5·0 g. from 10·0 g. of the naphthylamine (Found: Loss at 160°, 14·4; Na, 11·0. $C_{21}H_{12}O_{13}N_2S_4Na_4,7H_2O$ requires H_2O, 14·9; Na, 10·9%). This *carbamide* retains chloride with persistency. It crystallises well in clusters of long needles and is very soluble in water.

s-*Carbamide of* m-*Aminobenzoyl*-2-*naphthylamine*-5 : 7-*disulphonic Acid*.—The amino-compound (10 g.) was phosgenated twice as described in the preceding paragraph. The partial separation of leaflets was completed by saturation with sodium chloride. The product after neutralisation was twice crystallised from hot water by addition of 3 volumes of alcohol (yield, 9·9 g.) (Found: Loss at 160°, 22·1; Na, 7·3. $C_{35}H_{22}O_{15}N_4S_4Na_4,15H_2O$ requires H_2O, 22·0; Na, 7·5%). This *carbamide* is very soluble in water, crystallising therefrom in pointed leaflets, and is precipitated by sodium chloride in microscopic rods or narrow leaflets. Addition of concentrated hydrochloric acid to a warm solution precipitates leaflets, possibly of a free sulphonic acid. The *barium* salt is sparingly soluble and crystallises in leaflets.

s-*Carbamide of* m'-*Aminobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-5 : 7-*disulphonic Acid*.—Five g. of the amino-compound in 500 c.c. of water were phosgenated in the usual way. The resultant acid product consisted of an opalescent jelly similar to raw white of egg. It was optically anisotropic and devoid of visible particles. When neutralised, it became definitely biphasic to the eye with separation of the sodium salt. Separation was completed by addition of sodium chloride. The product was collected, dissolved in 120 c.c. of boiling water, and treated with 120 c.c. of alcohol. If the alcohol be omitted, the solution sets to a clear anisotropic gel. The product from 50% alcohol was amorphous (yield 3·6 g.) (Found: Loss at 160°, 10·3; Na, 6·5. $C_{49}H_{32}O_{17}N_6S_4Na_4,8H_2O$ requires H_2O, 10·7; Na, 6·9%). This *carbamide* is readily precipit-

ated, possibly as the free sulphonic acid, by concentrated hydrochloric acid as a crystalline liquid, but from more dilute solutions, at first as a clear anisotropic gel but later in discrete crystalline growths. If the solution be heated and allowed to cool, it deposits circular tufts of leaflets. The *calcium* and *barium* salts are both sparingly soluble.

m-*Nitrobenzoyl*-2-*naphthylamine*-4 : 8-*disulphonic Acid*.—C-Acid (12·0 g = 9·7 g. of anhydrous monosodium salt) in 210 c.c. of water was nitrobenzoylated in the usual way. The solid which had separated was collected, dissolved in the minimum volume of water (900 c.c.), acidified, and extracted with ether. On neutralisation to litmus, the nitro-amide (12·8 g.) separated in a crystalline condition. The mother-liquors and the original mother-liquors of the benzoylation gave a further 2·5 g. on concentration. The solid crystallised from 9 volumes of boiling water in clusters of soft, pale yellow needles (Found: Loss at 160°, 15·2; Na, 7·6. $C_{17}H_{10}O_9N_2S_2Na_2,5H_2O$ requires H_2O, 15·4; Na, 7·8%). The most striking property of the salt is the ease with which it is salted out from aqueous solutions. Such solutions are neutral to litmus and give no precipitate with hydrochloric acid.

m-*Aminobenzoyl*-2-*naphthylamine*-4 : 8-*disulphonic Acid*.—The preceding nitro-amide (equivalent to 9·9 g. of anhydrous salt) was dissolved in 275 c.c. of water and reduced with ferrous chloride and alkali at room temperature. The alkaline extracts of the ferric hydroxide on neutralisation to Congo-paper deposited the main bulk of the required amino-acid, and the mother-liquors on concentration gave a further small quantity (yield, practically quantitative). It crystallised from the minimum volume of boiling water as a voluminous mass of soft, silky needles (Found: Loss at 160°, 18·6; Na, 4·3. $C_{17}H_{13}O_7N_2S_2Na,5\frac{1}{2}H_2O$ requires H_2O, 18·2; Na, 4·2%). This *sodium hydrogen* salt is sparingly soluble in cold water, yielding a solution neutral to litmus. In dilute hydrochloric acid, it gives a sparingly soluble *diazosulphonate*, which separates in anisotropic, filamentous growths. The *disodium* salt was obtained by dissolving the hydrogen salt in a little water with the aid of sufficient sodium hydrogen carbonate to make the reaction faintly alkaline to litmus. It crystallised in fine needles, but it also occurs in plates. It is soluble in 10 volumes of water at room temperature (Found: Loss at 160°, 22·8. $C_{17}H_{12}O_7N_2S_2Na_2,7\frac{1}{2}H_2O$ requires H_2O, 22·5%. Found in anhydrous salt: Na, 9·7. $C_{17}H_{12}O_7N_2S_2Na_2$ requires Na, 9·9%).

m′-*Nitrobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-4 : 8-*disulphonic Acid*.—The foregoing acid (10·2 g.) in 320 c.c. of water was nitrobenzoylated in the usual way. The final solution was clear, very viscous, and anisotropic. It was diluted with 400 c.c. of water,

acidified to Congo-paper, and extracted with ether. It was then neutralised to litmus, which restored the anisotropic gel condition. If the solution was more dilute, a gel was not formed, but anisotropic worm- or thread-like growths separated in quantity. These showed the phenomenon of black crosses under the polarising microscope, especially at the ends of growth. In either case, the solution was heated in the boiling water-bath and saturated with sodium chloride with stirring. When cold, the precipitated gelatinous solid was collected in quantitative yield, without washing. 5 G. of the air-dried material were dissolved in 75 c.c. of hot water and treated with 20 c.c. of concentrated hydrochloric acid. The solution rapidly deposited a thick felt of needles. These were filtered off, dissolved in 25 c.c. of hot water, and heated with 10 c.c. of concentrated hydrochloric acid. Fine, long needles rapidly separated, which were filtered off as dry as possible, rubbed on porous plate, and dried in a vacuum over sulphuric acid and sodium hydroxide. In this way, 2·35 g. of almost pure, anhydrous *disulphonic acid* were obtained free from chloride (Found: Na, 0·4%. 0·249 G. was equivalent to 8·2 c.c. of *N*/10-sodium hydroxide, agreeing with the value required for a mixture of 95% of disulphonic acid and 5% of disodium salt). A repetition of the procedure would probably remove the last traces of sodium. The disulphonic acid, treated with a little water, swells up, forming a clear, viscous, anisotropic fluid in equilibrium with the surrounding aqueous solution. More dilute solutions are clear and set to an anisotropic gel on addition of silver nitrate. If the crude crystalline disulphonic acid obtained after one treatment of the crude disodium salt with hydrochloric acid be dissolved in a small volume of hot water and treated with an equal volume of alcohol, the neutral *disodium* salt separates in soft balls of extremely minute needles (Found: Loss at 160°, 12·7. $C_{24}H_{15}O_{10}N_3S_2Na_2,5H_2O$ requires H_2O, 12·8%. Found in anhydrous salt: Na, 7·4. $C_{24}H_{15}O_{10}N_3S_2Na_2$ requires Na, 7·5%). The mother-liquors, however, are strongly acid to Congo-paper. This salt may be obtained directly from the original crude disodium salt by dissolving it in hot water and adding alcohol, but the process through the disulphonic acid is preferable. The disodium salt is moderately easily soluble in cold water and on addition of a little sodium chloride the solution sets to a clear anisotropic gel, a state also obtained by dissolving the disodium salt in warm water and allowing the solution to cool. This gel remains unchanged in a sealed vessel for many months. The *barium* and *calcium* salts are very sparingly soluble, the former crystallising in hairs. The *magnesium* salt crystallises in clusters of needles moderately easily soluble in water.

m'-*Aminobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-4:8-*disulphonic Acid*.—The foregoing disodium salt (7·6 g.) in 250 c.c. of water was reduced with ferrous chloride and alkali at 25°. The filtrate and alkaline extracts of the ferric hydroxide were made faintly acid to Congo-paper; the amino-compound then separated as a voluminous, anisotropic, gelatinous product which, on filtration, was left as a white, soapy solid. It was dissolved in 350 c.c. of boiling water and treated with an equal volume of alcohol; it then separated slowly in gelatinous, oat-shaped, anisotropic crystals (yield, 6·15 g.) (Found: Loss at 160°, 17·1; Na, 3·3. $C_{24}H_{18}O_8N_3S_2Na,6\frac{1}{2}H_2O$ requires H_2O, 17·2; Na, 3·4%). This *sodium hydrogen* salt is sparingly soluble in hot water, and a boiling saturated aqueous solution when allowed to cool gives two phases, a clear supernatant liquor and anisotropic aggregates simulating ill-formed, crystalline growths. On filtration on hardened paper under pressure, both phases passed through, yielding a macroscopically homogeneous filtrate with a crystalline sheen. Examined microscopically, it showed complete absence of particles, the whole fluid being anisotropic under polarised light. On prolonged centrifuging there is a separation of a clear aqueous upper layer and a more uniform orientation of the sheen in spiral form in the lower layer.

s-*Carbamide of* 2-*Naphthylamine*-4:8-*disulphonic Acid*.—This carbamide was prepared by a double phosgenation of the parent amine (5·0 g.), separation being completed by addition of sodium chloride. After neutralisation it was twice crystallised from water and separated in clusters of microscopic needles (yield, 3·5 g.) (Found: Loss at 160°, 11·3; Na, 11·1. $C_{21}H_{12}O_{13}N_2S_4Na_4,5H_2O$ requires H_2O, 11·1; Na, 11·3%). This *carbamide* is soluble in water at room temperature to the extent of 5%. It is not very readily salted out and is not precipitated by concentrated hydrochloric acid.

s-*Carbamide of* m-*Aminobenzoyl*-2-*naphthylamine*-4:8-*disulphonic Acid*.—For the preparation of this carbamide, 80 volumes of water were required and a double phosgenation was necessary. At the end of the phosgenation the crude carbamide separated in the liquid crystalline state, in the form of stringy, anisotropic masses. After saturation with sodium chloride, the product could be filtered off on hardened paper and after neutralisation with alkali it was dissolved in 9 volumes of hot water and treated with an equal volume of alcohol. The carbamide separated on keeping in clusters of small needles. The yield was 10·5 g. from 10·0 g. of initial material (Found: Loss at 160°, 18·4; Na, 7·5. $C_{35}H_{22}O_{15}N_4S_4Na_4,12H_2O$ requires H_2O, 18·4; Na, 7·8%). This *carbamide* is readily soluble in water, is fairly readily salted out, and is precipitated by excess

of concentrated hydrochloric acid in the liquid crystalline state; if, however, the solution be warmed and allowed to cool slowly, the carbamide separates in discrete crystalline growths. The *calcium* and *barium* salts are sparingly soluble, the latter notably so.

s-*Carbamide of* m′-*Aminobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-4 : 8-*disulphonic Acid.*—The parent amine (5 g.) was phosgenated in the usual way, and precipitation of the crude product completed by addition of sodium chloride. It was dissolved in 30 c.c. of boiling water, neutralised, and treated with 70 c.c. of alcohol. On keeping, the carbamide separated without definite recognisable structure, but the product was anisotropic (yield, 4·7 g.) (Found : Loss at 160°, 18·2; Na, 5·7, 6·1. $C_{49}H_{32}O_{17}N_6S_4Na_4,14\frac{1}{2}H_2O$ requires H_2O, 17·9; Na, 6·3%). This *carbamide* is soluble in water and crystallises from concentrated solutions in microscopic, circular, crystalline aggregates. It is readily precipitated, possibly as the free tetrasulphonic acid, by addition of concentrated hydrochloric acid in a similar crystalline form. The *magnesium*, *barium*, and *calcium* salts are sparingly soluble.

m-*Nitrobenzoyl*-2-*naphthylamine*-6 : 8-*disulphonic Acid.*—G-Acid (9·8 g. of anhydrous sodium hydrogen salt) in 120 c.c. of water was nitrobenzoylated in the usual way. The solution was diluted with 425 c.c. of water to dissolve the solid which had separated; it was then acidified and extracted with ether. After neutralisation the solution was concentrated at 50° and the successive crops of gelatinous solid were collected without washing. The combined crops were made up to 150 c.c. with boiling water, and 150 c.c. of alcohol added. On keeping, the nitro-amide separated in soft, woolly needles (yield, 14·55 g.) (Found : Loss at 160°, 19·9; Na, 7·7. $C_{17}H_{10}O_9N_2S_2Na_2,7H_2O$ requires H_2O, 20·3; Na, 7·4%). This *amide* is readily soluble in hot water and separates on cooling as an anisotropic, gelatinous phase, possibly a semi-rigid liquid crystalline phase, as it flowed when submitted to pressure under a coverslip. Addition of concentrated hydrochloric acid gave an anisotropic gelatinous precipitate, as also did the addition of sodium chloride, which even in small quantities has a salting-out effect.

m-*Aminobenzoyl*-2-*naphthylamine*-6 : 8-*disulphonic Acid.*—The foregoing nitro-compound (12·4 g.) in 250 c.c. of water was reduced with ferrous chloride and alkali at 25°. On acidification, the filtrate and alkaline extracts of the ferric hydroxide gave a crystalline precipitate, and the mother-liquors on concentration a further small crop. These were dissolved in 50 c.c. of boiling water and treated with 20 c.c. of alcohol. The amide separated on cooling as a compact mass of needles (yield, 8·8 g.) (Found : Loss at 160°, 18·2. $C_{17}H_{13}O_7N_2S_2Na,5\frac{1}{2}H_2O$ requires H_2O, 18·2%. Found in anhydrous

solid: Na, 5·1. $C_{17}H_{13}O_7N_2S_2Na$ requires Na, 5·2%). This *amide* is readily soluble in hot water. A hot concentrated solution, when cold, becomes transformed into a viscous liquid crystalline mass with a sheen. This remains unchanged when kept in a stoppered tube for months. The amide forms a sparingly soluble *diazo-compound*, crystallising in needles with a primrose-yellow colour.

m′-*Nitrobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-6 : 8-*disulphonic Acid*.—The preceding amino-compound (16·3 g.) in 370 c.c. of water was nitrobenzoylated in the usual way. The very viscous solution which resulted was acidified and mixed with an equal volume of alcohol. On keeping at 0°, the precipitate crystallised (yield, 19·5 g.). It separated from hot 65% alcohol in minute, soft needles (Found: Loss at 160°, 14·7. $C_{24}H_{15}O_{10}N_3S_2Na_2,6H_2O$ requires H_2O, 14·9%. Found in anhydrous solid: Na, 7·2. $C_{24}H_{15}O_{10}N_3S_2Na_2$ requires Na, 7·5%). This *amide* is soluble in 14 parts of boiling water and separates in anisotropic gelatinous globules. If the amide be left in contact with 18 volumes of water, the original white powder disappears and the whole of the fluid becomes a white elastic mass with a sheen. Under the polarising microscope it retained the anisotropic sheen and flowed under uneven pressure of the cover-slip. A hot solution treated with concentrated hydrochloric acid deposits a microcrystalline precipitate, possibly of the free disulphonic acid. The amide is very readily salted out and gives sparingly soluble precipitates with calcium, magnesium, and barium chlorides.

m′-*Aminobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-6:8-*disulphonic Acid*.—The preceding nitro-amide (17·4 g.) was dissolved in 600 c.c. of water at 30° and treated with 84 c.c. of 2*N*-sodium hydroxide. The solution set to a clear anisotropic gel, which gradually disintegrated on addition of 33·6 g. of ferrous chloride in 50 c.c. of water. Finally, a further 84 c.c. of 2*N*-sodium hydroxide were added, the final reaction being made faintly alkaline to litmus. After being stirred for 1 hour, the solution was warmed to 50° to ensure complete solution and reduction of the nitro-compound. The filtrate and alkaline extracts of the ferric hydroxide on acidification deposited the amino-compound in soft, matted, microscopic needles. Precipitation was completed by addition of sodium chloride. The collected solid was dissolved in the minimum volume (700 c.c.) of boiling water and treated with 350 c.c. of alcohol; on cooling, the amino-amide crystallised in clusters of soft, white needles (yield, 14·7 g.) (Found: Loss at 160°, 14·5; Na, 3·5. $C_{14}H_{18}O_8N_3S_2Na,5\frac{1}{2}H_2O$ requires H_2O, 15·0; Na, 3·5%). This *amino*-compound is soluble in boiling water; the solution, on cooling, develops a white sheen, due to separation of the liquid crystalline phase. If a small amount of

sodium chloride be added to a clear dilute solution, this develops the liquid crystalline sheen, but only temporarily, the amide separating eventually in the solid crystalline condition. Hydrochloric acid also precipitates a liquid crystalline phase, and in very dilute hydrochloric acid a clear solution gives a liquid crystalline *diazosulphonate* on addition of sodium nitrite. The *disodium* salt is readily obtained as well-formed needles by dissolving the sodium hydrogen salt in warm sodium hydrogen carbonate solution and allowing it to cool. The *magnesium*, *calcium*, and *barium* salts are sparingly soluble in water.

s-*Carbamide of* 2-*Naphthylamine*-6 : 8-*disulphonic Acid*.—G-Acid (5 g.) was submitted to a thrice-repeated phosgenation under the usual conditions, sodium carbonate (20 mols.) being used each time. Separation of the solid was completed by addition of sodium chloride. After neutralisation it crystallised from boiling water, in which it was very soluble, in fine, colourless needles (Found : Loss at 160°, 19·9. $C_{21}H_{12}O_{13}N_2S_4Na_4,10H_2O$ requires H_2O, 20·0%. Found in the dried salt : Na, 12·6. $C_{21}H_{12}O_{13}N_2S_4Na_4$ requires Na, 12·8%). This *carbamide* has a sweet taste. It is readily soluble in water and is very readily salted out, in needles. It gives a sparingly soluble *barium* salt and with concentrated hydrochloric acid a precipitate of fine needles, probably the free tetrasulphonic acid.

s-*Carbamide of* m-*Aminobenzoyl*-2-*naphthylamine*-6 : 8-*disulphonic Acid*.—The parent amino-compound (5 g.) was submitted to a treble phosgenation. Separation of the solid, which consisted of very fine, small needles, was completed by saturation with sodium chloride. The product was dissolved in 50 c.c. of hot water and neutralised. It separated in round, weakly anisotropic nodules, which coalesced on attempted washing. It was redissolved in 25 c.c. of water, and 25 c.c. of alcohol added ; it then slowly separated in clusters of needles (yield 3·5 g.) (Found in substance crystallised from water : Loss at 160°, 19·8. $C_{35}H_{22}O_{15}N_4S_4Na_4,13H_2O$ requires H_2O, 19·6%. Found in anhydrous salt : Na, 10·0. $C_{35}H_{22}O_{15}N_4S_4Na_4$ requires Na, 9·6%). This *carbamide* is very readily salted out. It gives sparingly soluble salts with magnesium, calcium, and barium chlorides. With concentrated hydrochloric acid it gives a precipitate of needles, probably the free tetrasulphonic acid.

s-*Carbamide of* m'-*Aminobenzoyl*-m-*aminobenzoyl*-2-*naphthylamine*-6 : 8-*disulphonic Acid*.—The parent amino-compound (5 g.) was submitted to a double phosgenation. Separation of the carbamide was completed by addition of sodium chloride. It was then dissolved in 150 c.c. of boiling water with the aid of sufficient alkali to adjust the reaction to neutrality. To the hot solution 150 c.c.

of alcohol were added and on keeping the carbamide separated. It was again crystallised from 100 c.c. of water and 325 c.c. of alcohol (yield, 3·8 g.) (Found: Loss at 160°, 19·9. $C_{49}H_{32}O_{17}N_6S_4Na_4,16\frac{1}{2}H_2O$ requires H_2O, 19·9%. Found in anhydrous salt: Na, 7·6. $C_{49}H_{32}O_{17}N_6S_4Na_4$ requires Na, 7·7%). This *carbamide* separates from water–alcohol mixtures in weakly anisotropic, gelatinous particles. It is soluble in water; a hot concentrated solution on cooling deposits circular anisotropic clusters, but the surrounding aqueous medium also is anisotropic and flows under pressure of a cover-slip. Crystallisation of the solid phase proceeds at the expense of the liquid crystalline phase. Addition of dilute hydrochloric acid to a solution of the carbamide gives a clear anisotropic gel. The *magnesium*, *calcium*, and *barium* salts are sparingly soluble.

1-m-*Nitrobenzoylamino*-8-*naphthol*-3 : 6-*disulphonic Acid*.—H-Acid (14·7 g.) was suspended in 70 c.c. of water with addition of 5·5 g. of hydrated sodium acetate (1 mol.) and nitrobenzoylated as described for earlier members. After acidification to Congo-paper, the heavy crop of crystals was collected, dried, and extracted with ether, leaving 18·2 g. of crude amide. The mother-liquors gave a further 2·6 g. on concentration. These combined crops were dissolved in boiling water and treated with a quarter of its volume of alcohol. On keeping, the pure amide separated in compact clusters of needles (Found: Loss at 120°, 19·3. $C_{17}H_{10}O_{10}N_2S_2Na_2,7H_2O$ requires H_2O, 19·7%. Found in anhydrous salt: Na, 8·9. $C_{17}H_{10}O_{10}N_2S_2Na_2$ requires Na, 9·0%). This *amide* is readily soluble in warm water and is not precipitated by concentrated hydrochloric acid. It is only salted out with difficulty and separates in a crystalline state. The *barium* salt, tufts of needles, is readily soluble in warm water but much less soluble in cold.

1-m-*Aminobenzoylamino*-8-*naphthol*-3 : 6-*disulphonic Acid*.—The foregoing nitro-amide (12·8 g.) was reduced with ferrous chloride and alkali at 0° in the usual way. The filtrate and alkaline extracts of the ferric hydroxide on neutralisation gave a copious crystalline precipitate, which was collected, dissolved in 200 c.c. of boiling water, and treated with 100 c.c. of alcohol. After an interval, the pure amino-compound separated in delicate needles (yield, 9·3 g.) (Found: Loss at 160°, 17·4. $C_{17}H_{13}O_8N_2S_2Na,5H_2O$ requires H_2O, 16·4%. Found in dried salt: Na, 4·7. $C_{17}H_{13}O_8N_2S_2Na$ requires Na, 5·0%). This *sodium hydrogen* salt is not very soluble in warm water and it separates in anisotropic gelatinous particles. A dilute aqueous solution gives an immediate anisotropic precipitate on addition of dilute hydrochloric acid, probably of the disulphonic acid, which separates in microscopic leaflets if the solution be warmed

and allowed to cool. The *calcium*, *magnesium*, and *barium* salts are sparingly soluble, gelatinous precipitates. The *disodium* salt is very soluble in water and crystallises in needles.

1-m′-*Nitrobenzoyl*-m-*aminobenzoylamino*-8-*naphthol*-3 : 6-*disulphonic Acid*.—The foregoing amino-compound (10·7 g.) was nitrobenzoylated as described at the previous stage. The resulting solution consisted of a viscous syrup containing anisotropic stringy or worm-like masses in suspension. It was diluted with 2000 c.c. of water, acidified, and extracted with ether. The solution was neutralised and then set to a clear anisotropic gel. It liquefied on rise of temperature and was concentrated at 50° to one-half its bulk and acidified with 200 c.c. of concentrated hydrochloric acid. This caused the precipitation of anisotropic liquid threads from which the mother-liquor could be decanted. When these were dissolved in hot water (140 c.c.) and treated with 280 c.c. of alcohol, the required salt separated in a filterable condition (yield, 11·8 g.) (Found : Loss at 160°, 17·4. $C_{24}H_{15}O_{11}N_3S_2Na_2,7\frac{1}{2}H_2O$ requires H_2O, 17·6%. Found in dried salt : Na, 7·3. $C_{24}H_{15}O_{11}N_3S_2Na_2$ requires Na, 7·3%). This *disodium* salt is soluble in boiling water and, on cooling, separates in anisotropic, worm-like growths. A dilute aqueous solution treated with a little sodium chloride sets to a clear anisotropic gel. Under the most favourable conditions for crystallisation—a little water and excess of alcohol—it separates in anisotropic, gelatinous aggregates devoid of recognisable structure.

1-m′-*Aminobenzoyl*-m-*aminobenzoylamino*-8-*naphthol*-3 : 6-*disulphonic Acid*.—The preceding nitro-compound (9·0 g.) was reduced at 0° with ferrous chloride and alkali. The filtrate and alkaline extracts of the ferric hydroxide were neutralised to Congo-paper and on being kept for 24 hours deposited almost the whole of the amino-compound as an amorphous precipitate. This was dissolved in 100 c.c. of boiling water and treated with 50 c.c. of alcohol; it then separated slowly in the amorphous condition (Found : Loss at 160°, 16·9. $C_{24}H_{18}O_9N_3S_2Na,6\frac{1}{2}H_2O$ requires H_2O, 16·8%. Found in anhydrous salt : Na, 4·3. $C_{24}H_{18}O_9N_3S_2Na$ requires Na, 4·0%). This *sodium hydrogen* salt is not very soluble in boiling water. It separates on cooling in microscopic spicules or leaflets. Its dilute aqueous solution is precipitated by concentrated hydrochloric acid as a gelatinous, anisotropic product, which dissolves on warming and then crystallises in fine needles. It gives an orange colour on diazotisation.

ON-*Carbonyl*-1 : 8-*aminonaphthol*-3 : 6-*disulphonic Acid*.—H-Acid (5 g.) was dissolved in 100 c.c. of water containing 10 c.c. of 2*N*-sodium hydroxide and 20 g. of anhydrous sodium carbonate. The solution was phosgenated till acid to Congo-paper. The solid was

collected and crystallised from hot water (40 c.c.) (yield, 4 g.) (Found: Loss at 150°, 16·1. $C_{11}H_5O_8NS_2Na_2,4H_2O$ requires H_2O, 15·6%. Found in dried salt: Na, 11·8. $C_{11}H_5O_8NS_2Na_2$ requires Na, 11·8%). This *disodium* salt is soluble in 10 parts of cold water to a neutral solution. It crystallises in needles which darken on exposure to the air. It is readily salted out by sodium chloride and gives a very sparingly soluble *barium* salt. Unlike all the other derivatives of H-acid described in this paper, which give an intense magenta-red colour with Pauly's reagent in sodium carbonate solution, this salt gives no coloration.

s-*Carbamide of* 1-m-*Aminobenzoylamino*-8-*naphthol*-3 : 6-*disulphonic Acid*.—Five g. of the aminobenzoylamide were submitted to a double phosgenation as described in previous instances. The precipitated solid was collected, dissolved in 15 c.c. of boiling water, neutralised, and treated with 7 c.c. of alcohol. The carbamide separated in clusters of gelatinous leaflets (yield, 3·0 g.) (Found: Loss at 160°, 19·8. $C_{35}H_{22}O_{17}N_4S_4Na_4,13\frac{1}{2}H_2O$ requires H_2O, 19·7%. Found in anhydrous salt: Na, 9·2. $C_{35}H_{22}O_{17}N_4S_4Na_4$ requires Na, 9·3%). This *carbamide* is soluble in boiling water and crystallises, on cooling, in the same way as from dilute alcohol. A solution in dilute nitric acid gives an orange-red solution on boiling. With magnesium, calcium, and barium chlorides it yields sparingly soluble, gelatinous precipitates.

s-*Carbamide of* 1-m′-*Aminobenzoyl*-m-*aminobenzoylamino*-8-*naphthol*-3 : 6-*disulphonic Acid*.—Five g. of the amino-compound were phosgenated in the usual way. The solution was saturated with sodium chloride, and the solid collected. It was dissolved in 260 c.c. of boiling water, neutralised, and treated with 200 c.c. of alcohol. The carbamide separated in gelatinous particles which were isotropic (yield, 3·3 g.) (Found: Loss at 160°, 20·6; Na, 6·0. $C_{49}H_{32}O_{19}N_6S_4Na_4,17\frac{1}{2}H_2O$ requires H_2O, 20·4; Na, 6·0%). This *carbamide* is not very soluble in water. It is readily salted out and gives sparingly soluble salts with magnesium, barium, and calcium chlorides.

2-m-*Nitrobenzoylamino*-8-*naphthol*-3 : 6-*disulphonic Acid*.—2R-Acid (24·2 g. of commercial disodium salt) was dissolved in 150 c.c. of water and nitrobenzoylated in the usual way. The highly coloured but clear solution was acidified to Congo-paper and on being kept for 12 hours at 0° gave 37 g. of crystalline solid, which, on ether extraction, gave 27·0 g. of amide. The original aqueous liquors after extraction with ether and concentration gave a further 4·2 g. of amide. The combined crops crystallised from 100 c.c. of water in small prisms (yield, 25·2 g.) (Found: Loss at 160°, 13·6. $C_{17}H_{10}O_{10}N_2S_2Na_2,4\frac{1}{2}H_2O$ requires H_2O, 13·7%. Found in anhydr-

ous salt: Na, 8·7. $C_{17}H_{10}O_{10}N_2S_2Na_2$ requires Na, 9·0%). This *disodium* salt is readily soluble in hot water but sparingly soluble in cold. It forms a *barium* salt, sparingly soluble in water, which crystallises in microscopic clusters of needles. This amide is readily salted out; it gives an eosin-like colour in sodium carbonate solution with Pauly's reagent. When boiled with dilute nitric acid it gives an orange-red solution.

2-m-*Aminobenzoylamino*-8-*naphthol*-3 : 6-*disulphonic Acid*.—The above-described nitro-compound (20·8 g.) was reduced at 0° with ferrous chloride and alkali in the usual way. The filtrate and alkaline extracts of the ferric hydroxide on neutralisation to Congo-paper deposited 16·8 g. of small needles. The mother-liquor on concentration gave a further 2·1 g. The product was recrystallised from 10 volumes of boiling water (Found: Loss at 160°, 13·6. $C_{17}H_{13}O_8N_2S_2Na,4H_2O$ requires H_2O, 13·5%. Found in anhydrous salt: Na, 4·7. $C_{17}H_{13}O_8N_2S_2Na$ requires Na, 5·0%). This *amide* has a faint acid reaction to Congo-paper. It forms a *diazosulphonate*, fine needles, and it gives a sparingly soluble *barium* salt, granular crystals. It is very readily salted out.

2-m′-*Nitrobenzoyl*-m-*aminobenzoylamino*-8-*naphthol*-3 : 6-*disulphonic Acid*.—The preceding amino-compound (10·6 g.) in 100 c.c. of water was nitrobenzoylated by the usual process. The final product was a clear anisotropic gel. Addition of a little concentrated hydrochloric acid gave a limpid fluid, but excess gave a clear anisotropic gel. This was stirred with sodium chloride; it then coagulated and could be filtered. It was dissolved in 150 c.c. of boiling water and treated with 400 c.c. of alcohol. On keeping, the nitro-compound separated in the amorphous state, but gradually transformed into clusters of microscopic needles (yield, 11·5 g.) (Found in product from 50% alcohol: Loss at 160°, 17·1. $C_{24}H_{15}O_{11}N_3S_2Na_2,7H_2O$ requires H_2O, 16·7%. Found in dried salt: Na, 7·2. $C_{24}H_{15}O_{11}N_3S_2Na_2$ requires Na, 7·3%). This *nitro-compound* is best obtained white and in needles by stirring it with just insufficient boiling water to dissolve it and adding alcohol gradually to complete its solution and then several volumes of alcohol. The *calcium* and *barium* salts are sparingly soluble.

2-m′-*Aminobenzoyl*-m-*aminobenzoylamino*-8-*naphthol*-3 : 6-*disulphonic Acid*.—The foregoing nitro-compound (12·0 g.) was dissolved in 222 c.c. of 0·5*N*-sodium hydroxide and reduced with ferrous chloride and alkali at 15° in the usual way. The filtrate and alkaline extracts of the ferric hydroxide were acidified and separation of the anisotropic solid was completed by saturation with sodium chloride. The gelatinous solid obtained on filtration was dissolved in 100 c.c. of boiling water and treated with 300 c.c. of

alcohol. On keeping at 0° for some days, a gelatinous, anisotropic mass filled the fluid. This was collected by filtration and washed free from chloride by 90% alcohol. The mother-liquors were concentrated to a small volume and re-treated in a similar way. The total yield of solid, dried in a vacuum, was 9·0 g. (Found: Loss at 160°, 20·6. $C_{24}H_{18}O_9N_3S_2Na,8\frac{1}{2}H_2O$ requires H_2O, 20·9%. Found in dried salt: Na, 4·3. $C_{24}H_{18}O_9N_3S_2Na$ requires Na, 4·0%). This *amino-compound* is readily soluble in hot water and separates on cooling in gelatinous, anisotropic needles. It is very readily salted out and if such a solution be warmed until clear and be allowed to cool, it sets to a clear anisotropic gel. A dilute solution in hydrochloric acid gives a clear anisotropic, gelatinous solution on addition of sodium nitrite and the product couples with alkaline β-naphthol. Hot dilute nitric acid gives a red coloration, and an alkaline solution couples with diazotised sulphanilic acid with production of an eosin-like coloration.

s-*Carbamide of* 2 : 8-*Aminonaphthol*-3 : 6-*disulphonic Acid*.—2R-Acid (5·0 g.) in 250 c.c. of water containing 26 g. of anhydrous sodium carbonate was phosgenated until the reaction was acid to Congo-paper. The solution was neutralised and saturated with sodium chloride and on being kept for several days deposited the carbamide mixed with some unchanged amine. It was redissolved, submitted to a second phosgenation, and when the conditions were adjusted for its isolation it slowly separated. It crystallised from 2 volumes of boiling water in rods (yield, 45%) (Found: Loss at 160°, 19·2. $C_{21}H_{12}O_{15}N_2S_4Na_4,10H_2O$ requires H_2O, 19·3%. Found in dried salt: Na, 12·3. $C_{21}H_{12}O_{15}N_2S_4Na_4$ requires Na, 12·2%). This *carbamide* is readily soluble in water and is not readily salted out. It gives no precipitate with concentrated hydrochloric acid, whereas 2R-acid gives a precipitate of needles. Unlike 2R-acid, it gives a microcrystalline *barium* salt on addition of concentrated barium chloride solution.

s-*Carbamide of* 2-m-*Aminobenzoylamino*-8-*naphthol*-3 : 6-*disulphonic Acid*.—The parent amine (5·8 g.) was submitted to a double phosgenation in the usual way. The precipitated solid was dissolved in 17·5 c.c. of boiling water with neutralisation and precipitated by addition of an equal volume of alcohol (yield of material dried in a vacuum, 2·8 g.) (Found: Loss at 160°, 13·6. $C_{35}H_{22}O_{17}N_4S_4Na_4,8\frac{1}{2}H_2O$ requires H_2O, 13·4%. Found in dried solid: Na, 9·2. $C_{35}H_{22}O_{17}N_4S_4Na_4$ requires Na, 9·3%). This *carbamide* is readily soluble in water and crystallises from very concentrated solutions as a microcrystalline powder, but better by addition of sodium chloride. The *calcium* and *barium* salts are sparingly soluble.

s-*Carbamide of* 2-m′-*Aminobenzoyl*-m-*aminobenzoylamino*-8-*naphthol*-3 : 6-*disulphonic Acid.*—The parent amine (5 g.) in 100 volumes of water containing 20 g. of sodium carbonate was submitted to a double phosgenation at 30°. The precipitated solid was neutralised, dissolved in 120 c.c. of boiling water, and treated with 120 c.c. of absolute alcohol. The yield of material dried in a vacuum over sulphuric acid was 3·0 g. (Found: Loss at 160°, 11·9. $C_{49}H_{32}O_{19}N_6S_4Na_4,9H_2O$ requires H_2O, 11·7%. Found in dried solid: Na, 7·6. $C_{49}H_{32}O_{19}N_6S_4Na_4$ requires Na, 7·5%). This *carbamide* is easily soluble in warm water and is readily salted out as a weakly anisotropic solid. Concentrated hydrochloric acid precipitates a weakly anisotropic, finely divided substance, possibly the free tetrasulphonic acid. The *magnesium*, *calcium*, and *barium* salts are sparingly soluble, gelatinous substances.

m-*Nitrobenzoyl*-1-*naphthylamine*-4 : 6 : 8-*trisulphonic Acid.*—The parent naphthylaminetrisulphonic acid (9·0 g. of disodium salt) was nitrobenzoylated in the usual way. After removal of nitrobenzoic acid the neutralised liquors on concentration gave the required amide, which was recrystallised from a small volume of water (yield, 13·55 g.) (Found: Loss at 160°, 11·7. $C_{17}H_9O_{12}N_2S_3Na_3,4\frac{1}{2}H_2O$ requires H_2O, 11·9%. Found in dried substance: Na, 11·4. $C_{17}H_9O_{12}N_2S_3Na_3$ requires Na, 11·5%). This *amide* is very readily soluble in water and is only salted out with difficulty. It is best crystallised from diluted alcohol and then separates in clusters of needles. It forms a readily soluble *calcium* salt and a somewhat less soluble *barium* salt, crystallising in woolly needles.

m-*Aminobenzoyl*-1-*naphthylamine*-4 : 6 : 8-*trisulphonic Acid.*—13·3 G. of the above nitro-amide were reduced with ferrous chloride and alkali. The neutralised filtrates, freed from iron, were concentrated under reduced pressure at 80° and as much sodium chloride removed as possible by evaporation and filtration and precipitation with alcohol. The amino-compound was then precipitated as an oil by excess of alcohol and gradually solidified. The yield of crude material containing some sodium chloride was 11·1 g. It was not obtained sufficiently pure for analysis. It is extremely soluble in water and is not salted out. It is also soluble in hot methyl alcohol. It diazotises and then couples with β-naphthol. From ethyl-alcoholic solutions containing a little water it crystallises in needles or prisms.

m′-*Nitrobenzoyl*-m-*aminobenzoyl*-1-*naphthylamine*-4 : 6 : 8-*trisulphonic Acid.*—8 G. of the above amino-compound were nitrobenzoylated in the usual way. The neutralised liquor on concentration deposited a felted mass of needles, which were collected

without washing, dissolved in 10 c.c. of hot water, and treated with 50 c.c. of alcohol. When cool, the required nitro-amide had separated as a felt of very fine needles (yield, 7·4 g.). For analysis, it was recrystallised from 90% alcohol (Found: Loss at 160°, 16·7. $C_{24}H_{14}O_{13}N_3S_3Na_3,8H_2O$ requires H_2O, 16·7%. Found in dried substance: Na, 9·4. $C_{24}H_{14}O_{13}N_3S_3Na_3$ requires Na, 9·6%). This *nitro-amide* is very easily soluble in water, but is readily salted out. On addition of calcium or barium chloride the *calcium* or *barium* salt is precipitated as a gelatinous, anisotropic product, but on keeping the barium salt crystallises in tufts of woolly needles.

m′-*Aminobenzoyl*-m-*aminobenzoyl*-1-*naphthylamine*-4 : 6 : 8-*trisulphonic Acid*.—The preceding nitro-compound (7·5 g.) was reduced at 0° with ferrous chloride in the usual way. The solution, neutralised to Congo-paper and free from iron, was concentrated to about 60 c.c.; it then set to a paste of fine, short needles. These were collected without washing, dissolved in 20 c.c. of hot water, and treated with 25 c.c. of absolute alcohol. The product separated as an anisotropic, gelatinous mass filling the solution. It was filtered off and well washed with 80% alcohol, but could not thus be freed from chloride. The yield of material dried in a vacuum was 4·5 g. This product is a *disodium* salt and can be salted out from aqueous solutions, but not very readily. For analysis it was dissolved in a small volume of hot water, neutralised to litmus, and treated with several volumes of alcohol. On keeping, the solution deposited balls of woolly needles of the *trisodium* salt (Found in material dried in a vacuum: Loss at 160°, 8·7. $C_{24}H_{16}O_{11}N_3S_3Na_3,3\frac{1}{2}H_2O$ requires H_2O, 8·4%. Found in anhydrous solid: Na, 9·6. $C_{24}H_{16}O_{11}N_3S_3Na_3$ requires Na, 10·0%). The trisodium salt is not salted out and is extremely readily soluble in water. If the reaction of the original liquors from the reduction be neutral to litmus instead of neutral or acid to Congo, no amino-compound separates until almost all the sodium chloride has been removed and the solution concentrated to a syrup.

s-*Carbamide of* 1-*Naphthylamine*-4 : 6 : 8-*trisulphonic Acid*.—The parent amine (10 g.) was phosgenated at 30° in a solution containing 100 g. of anhydrous sodium carbonate in 250 c.c. of water. The solution was neutralised and concentrated repeatedly under reduced pressure with intermediate removal of as much sodium chloride as possible. The residual filtrate was evaporated almost to dryness in a vacuum, treated with a few c.c. of warm water, and decanted from undissolved sodium chloride. On cooling, the carbamide separated in long, delicate needles, which were recrystallised from a little water. In this way, 4·1 g. of the carbamide were obtained, still containing some sodium chloride which could not be removed

from the limited quantities at our disposal. This *carbamide* is extremely readily soluble in water, is not salted out, and gives no precipitate on addition of concentrated hydrochloric acid or alkaline-earth chlorides.

s-*Carbamide of* m-*Aminobenzoyl*-1-*naphthylamine*-4 : 6 : 8-*trisulphonic Acid*.—The unisolated amino-compound prepared from 10 g. of the corresponding nitro-compound was made up to 500 c.c. with water and treated with 40 g. of anhydrous sodium carbonate, and carbonyl chloride passed in until the solution was acid. The neutralised solution was concentrated and as much sodium chloride removed as possible, first by direct crystallisation, then by addition of ethyl alcohol, and finally by addition of methyl alcohol. The liquor was then concentrated to a small volume and several volumes of methyl alcohol were added so long as there was precipitation of sodium chloride; after a few days, below 0°, the required carbamide separated in soft needles (yield, 6·8 g.). For analysis, it was recrystallised under the same conditions from 66% methyl alcohol at − 5° (Found in material dried in a vacuum : Loss at 160°, 6·1. $C_{35}H_{20}O_{21}N_4S_6Na_6,4H_2O$ requires H_2O, 5·8%. Found in dried solid : Na, 11·4. $C_{35}H_{20}O_{21}N_4S_6Na_6$ requires Na, 11·9%). This *carbamide* is hygroscopic and extremely readily soluble in water or in 98% methyl alcohol and is not salted out.

s-*Carbamide of* m′-*Aminobenzoyl*-m-*aminobenzoyl*-1-*naphthylamine*-4 : 6 : 8-*trisulphonic Acid*.—The base prepared from the nitro-compound (13·8 g. anhydrous) without isolation was phosgenated in 500 c.c. of water in presence of 50 g. of anhydrous sodium carbonate. The carbamide was isolated in the same way as the preceding member. The yield of crystalline solid containing a little chloride was 9·65 g. For analysis, it was dissolved in 10 c.c. of hot water and treated with 35 c.c. of 98% methyl alcohol; it then slowly crystallised, below 0°, in clusters of white needles. It was washed with 80% methyl alcohol, cooled to − 5° (yield, 8·1 g.). As it was hygroscopic, it was dried in a vacuum (Found : Loss at 160°, 9·3. $C_{49}H_{30}O_{23}N_6S_6Na_6,8H_2O$ requires H_2O, 9·3%. Found in dried solid : Na, 9·5. $C_{49}H_{30}O_{23}N_6S_6Na_6$ requires Na, 9·8%). This *carbamide* is very soluble in water or methyl alcohol and is not salted out. With saturated barium chloride solution, it gives after some delay a *barium* salt in anisotropic particles. It gives no precipitate with lead acetate, but is precipitated by basic lead acetate.

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CCCCVIII.—*Investigations on the Reactivity of Halogens in Various Types of Naphthalene Derivatives. Part I.*

By JOHN BALDWIN SHOESMITH and HANNES RUBLI.

A SERIES of investigations has been undertaken with the view of extending work already carried out on halogenated derivatives of benzene (J., 1922, **121**, 1391; 1923, **123**, 2828; 1924, **125**, 1312, 2278; 1926, 214, 2832; this vol., p. 1768) to the naphthalene series. It has been discovered that the ease of replacement of both nuclear and side-chain halogen in naphthalene compounds is markedly different from that in the corresponding benzene derivatives; thus, α- and β-naphthylmethyl bromides are both more readily hydrolysed in aqueous alcohol at 25° than is benzyl bromide, the order of ease of hydrolysis being α>β, a fact which substantiates the rule put forward by Olivier (*Rec. trav. chim.*, 1923, **42**, 775) showing the connexion between the rate of hydrolysis of benzyl halides and substitution in the aromatic nucleus. Owing to the rapidity of the hydrolysis, it was not possible to ascertain whether this order remained the same at higher temperatures, but it appeared to be so at 60°. The two isomerides are also almost equally more rapidly reduced than benzyl bromide at 77°.

Of the α- and β-bromo- and iodo-naphthalenes, only α-iodonaphthalene is appreciably reduced at 100° by hydrogen iodide, and it appears as if the halogen (especially iodine) attached to the nucleus in the position which is most readily attacked during substitution is correspondingly most readily removed by hydrogen iodide.

The reduction of 1-bromo-β-naphthol and 4-bromo-α-naphthol proved of interest in that (1) they are both very readily reduced, and (2) the order of ease of reduction is *o*>*p*, the reverse of the case in the corresponding benzene series. It has already been suggested (J., 1924, **125**, 1314) by one of us, and independently by Nicholet (*J. Amer. Chem. Soc.*, 1927, **49**, 1812), that the intermediate formation of molecules of a quinonoid type probably assists the reduction of such compounds, a suggestion borne out by the great reactivity of the ortho-compound above (since ortho-quinonoid forms are recognised as more prevalent in the naphthalene than in the benzene series), and also by the very slow rate of reduction of 5-bromo-α-naphthol in which the possibility of intervention of quinonoid formation is not so marked.

The formation of active quinonoid molecules is probably a powerful factor in the ease of reduction of the second series of nuclear-

halogenated naphthalene derivatives examined,* *viz.*, 1-bromo-2-methylnaphthalene and 4-bromo-1-methylnaphthalene, both of which are reduced by hydriodic acid at 100°, in contradistinction to the bromotoluenes, which are stable, and the order is again 1 : 2 > 1 : 4.

In various substituted α-naphthylmethyl bromides the reactivity of the bromine atoms was in the decreasing order *p*-OMe > *p*-CH_3 > unsubs. > *p*-Br, which is the same as in the hydrolysis of substituted benzyl bromides, the reciprocal of the time (in days) for 50% hydrolysis, which gives a measure of the velocity coefficient, being shown in parenthesis after each compound : *4-methoxy-α-naphthylmethyl bromide*(∞) > *4-methyl-α-naphthylmethyl bromide* (6·0) > α-naphthylmethyl bromide (0·55) > 4-bromo-α-naphthylmethyl bromide (0·29). 4-Methoxy-α-naphthylmethyl bromide resembles *p*-methoxybenzyl bromide in being almost instantaneously hydrolysed in aqueous alcohol, and its great reactivity, *e.g.*, in a moist atmosphere (see Experimental), must be due to the combined influences of the general and the powerful alternating effect of the methoxyl group, supplemented by a further effect due to the compound's "naphthalenoid" (as opposed to benzenoid) character. 4-Methyl-α-naphthylmethyl bromide also is very readily hydrolysed in aqueous alcohol, and the naphthalenoid enhancing influence is so great that in 2-methyl-α-naphthylmethyl bromide, in which a decreased reactivity might have been expected from steric hindrance, the bromine atom is almost as readily replaced as that in the 1 : 4-isomeride.

Whilst the hydrolysis of the methoxyl and methyl compounds proved to be too rapid to allow a satisfactory velocity coefficient to be obtained, the comparative slowness of the hydrolysis of the unsubstituted α- and β-naphthylmethyl bromides and of 4-bromo-α- and 1-bromo-β-naphthylmethyl bromides has enabled us to obtain a

TABLE I.

Compound.	$k \times 10^6$.	Compound.	$k \times 10^6$.
1. $C_{10}H_7 \cdot CH_2Br(\alpha)$	270	6. $Br(4) \cdot C_{10}H_6 \cdot CH_2Br(\alpha)$ ...	137
2. $C_{10}H_7 \cdot CH_2Br(\beta)$	210	7. $Br(1) \cdot C_{10}H_6 \cdot CH_2Br(\beta)$ ...	59
3. $C_6H_5 \cdot CH_2Br$	125	8. $Br(4) \cdot C_6H_4 \cdot CH_2Br(1)$ ...	71
4. $MeO(5) \cdot C_{10}H_6 \cdot CH_2Br(\alpha)$	485	9. $Br(2) \cdot C_6H_4 \cdot CH_2Br(1)$ ...	39
5. $Br(5) \cdot C_{10}H_6 \cdot CH_2Br(\alpha)$ ...	129		

numerical value of the increased reactivity, due to the compounds having acquired naphthalenoid characteristics in the α or β-position, by comparing the values in Table I (k = unimolecular velocity

* That formation of molecules of a quinonoid type might be intermediate in the reduction of the halogenated methylnaphthalenes appears probable in view of recent work of Schorigin (*Ber.*, 1926, **59**, 2504), who claims to have demonstrated the existence of the quinonoid modification of toluene.

coefficient at 25°). The ratio for compounds 1 and 3 is 2·16, and that for compounds 6 and 8 is 1·92; the reaction is therefore approximately twice as fast for the α-naphthalene derivatives as for the corresponding benzene derivatives. In the case of the β-naphthalene derivatives the increase is not so great, as may be seen from the ratio between Nos. 2 and 3 (1·68) and between Nos. 7 and 9 (1·52).

Definite evidence of the transmission of an influence from the 5- to the 1-position of the naphthalene nucleus has been obtained, in that the order of ease of hydrolysis of the following compounds is: *5-methoxy-α-naphthylmethyl bromide* ($k = 0{\cdot}000485$) > α-naphthylmethyl bromide ($k = 0{\cdot}000270$) > *5-bromo-α-naphthylmethyl bromide* ($k = 0{\cdot}000129$); it is important to note that this is the order of reactivity of the 1 : 4-isomerides, but whilst 4-methoxy-α-naphthylmethyl bromide is hydrolysed with great rapidity in aqueous-alcoholic solution, the 1 : 5-isomeride is comparatively slowly hydrolysed. This is in agreement with the generalisation of Olivier (*loc. cit.*), since α-naphthol in the form of its carbonate is brominated in the 4-position. The fact that the 5-methoxy-derivative is more reactive than the unsubstituted compound is of interest, and it is possible that in α-naphthol itself the 5-position is liable to attack, but the overwhelming reactivity of the 4-position completely masks the tendency to produce a 1 : 5-derivative.

The nuclear bromine atom in 5-bromo-α-naphthylmethyl bromide exercises a powerful retarding influence on the rate of hydrolysis of the lateral bromine atom, and the 1 : 4-isomeride ($k = 0{\cdot}000137$) is slightly but definitely more reactive than the 1 : 5-isomeride ($k = 0{\cdot}000129$), which is again in agreement with the production of more 1 : 4-dibromo- than 1 : 5-dibromo-naphthalene in the bromination of α-bromonaphthalene (Armstrong and Rossiter, *Chem. News*, 1892, **65**, 59).

The differences which exist between the hydrolysis of the 1 : 4- and 1 : 5-isomerides suggest that, whilst both alternating and general influences are readily transmitted from the 4- to the 1-position in naphthalene as in the corresponding benzene derivatives, the alternating influence does not readily pass from the 5- to the 1-position. An effect due to the general influence is apparent, *viz.*, the retarded reactivity of 5-bromo-α-naphthylmethyl bromide and the slightly enhanced reactivity of 5-methoxy-α-naphthylmethyl bromide as compared with the unsubstituted α-naphthylmethyl bromide, since bromine retards and methoxyl increases such reactivity in a general way (compare Shoesmith and Slater, J., 1926, 217).

EXPERIMENTAL.

The isomeric naphthylmethyl bromides were prepared by brominating the appropriate methylnaphthalene at the boiling point in direct sunlight. They were purified by crystallisation from alcohol; the α-isomeride had m. p. 53°, and the β- had m. p. 56°. They both possess lachrymatory properties, and produce a burning sensation on the skin.

4-Methoxy-α-naphthylmethyl Bromide.—4-Methoxy-α-naphthaldehyde, prepared from α-naphthyl methyl ether by Gattermann's method (*Annalen*, 1907, **357**, 365), was converted into 4-methoxy-α-naphthylcarbinol of m. p. 35° (*Anal. Fís. Quím.*, 1919, **17**, 125) by means of 66% aqueous potassium hydroxide (25% alcoholic potassium hydroxide was without action), and the carbinol, dissolved in dry benzene, was converted into the corresponding bromide by means of dry hydrogen bromide. The resulting yellow needles could not be recrystallised from any solvent owing to their great instability; they had m. p. 119—120° (decomp.) (Found: Br, hydrolysable, 24·7. $C_{12}H_{11}OBr,C_6H_6$ requires Br, 24·3%). The whole of this bromine became ionisable in 90% aqueous alcohol in 5 minutes. The yellow crystals fumed and rapidly liquefied in the atmosphere owing to hydrolysis.

An attempt to prepare 2-methoxy-α-naphthylcarbinol by a similar method was unsuccessful; 4-methoxy- and 2-methoxy-α-naphthoamides were found by Gattermann (*Annalen*, 1888, **244**, 72) to display analogous differences in their behaviour with potassium hydroxide; moreover 2-methoxy-α-naphthaldehyde gives anomalous results with Schiff's reagent. An attempt to obtain the carbinol by reduction of 2-methoxy-α-naphthaldoxime (by means of sodium amalgam in glacial acetic acid) to the corresponding amine also failed. This suggests that reactions involving the carbon atom of the aldehyde group are inhibited by the proximity of the methoxyl group on the one side and the additional ring system on the other.

An attempt was also made to prepare 3-methoxy-α-naphthylmethyl bromide, and the synthesis was carried as far as the corresponding alcohol, but insufficient of this was obtained for the purpose.

3-Methoxy-α-naphthaldehyde.—α-Naphthylamine-3 : 8-disulphonic acid (100 g.), dissolved in 1 l. of water containing 25 g. of sodium hydroxide, was reduced with 200 g. of 4% sodium amalgam, and the α-naphthylamine-3-sulphonic acid was converted into *3-methoxy-α-naphthaldehyde* by the methods already given (J., 1926, 3241). Especial care was necessary to ensure the absence of 3-hydroxy-α-naphthoic acid from the intermediate 3-methoxy-α-naphthoic acid; this was converted into *3-methoxy-α-naphthoyl chloride*, yellow

needles from light petroleum, m. p. 79° (Found: Cl, 15·5. $C_{12}H_9O_2Cl$ requires Cl, 16·1%), which was catalytically reduced. The aldehyde crystallises from light petroleum in colourless, rhombic plates, m. p. 60° (Found: C, 77·1; H, 5·4. $C_{12}H_{10}O_2$ requires C, 77·5; H, 5·4%); *oxime*, white needles from aqueous alcohol, m. p. 102°; *p-nitrophenylhydrazone*, brick-red needles from acetic acid, m. p. 197°; *semicarbazone*, white needles from aqueous alcohol, m. p. 200°. The yield of aldehyde is very small and only sufficient was obtained for characterisation and conversion as above into a small sample of *3-methoxy-α-naphthylcarbinol*. The carbinol crystallised from water in fine, colourless needles, m. p. 88° (Found: C, 76·1; H, 6·4. $C_{12}H_{12}O_2$ requires C, 76·5; H, 6·4%).

4-Bromo-α-naphthol was prepared by Reverdin and Kauffmann's method (*Ber.*, 1895, **28**, 3053) and, when purified by steam distillation in an atmosphere of nitrogen, was obtained as colourless needles, m. p. 129°. When the intermediate 4-bromo-α-naphthyl carbonate is treated in methyl-alcoholic solution alternately with 5% methyl-alcoholic potassium hydroxide and methyl sulphate in an atmosphere of nitrogen, *4-bromo-α-naphthyl methyl ether*, a colourless oil, b. p. 181°/18 mm. (Found: Br, 33·6. $C_{11}H_9OBr$ requires Br, 33·8%), may be obtained.

1-Bromo-β-naphthol, prepared by direct bromination of β-naphthol and repeatedly crystallised from acetic acid, had m. p. 84°.

1-Bromo-β- and 4-bromo-α-methylnaphthalenes were prepared by direct bromination of β- and α-methylnaphthalene, respectively, and purified by repeated fractionation in a vacuum. The samples used in the reduction experiments were free from hydrolysable bromine. They were converted into 1-bromo-β-naphthylmethyl bromide (m. p. 107°) and 4-bromo-α-naphthylmethyl bromide (m. p. 103°), respectively, by a current of dry bromine at 210—220°, and recrystallisation from light petroleum (Mayer and Sieglitz, *Ber.*, 1922, **55**, 1839).

4-Methyl-α-naphthylmethyl Bromide.—4-Bromo-1-methylnaphthalene (13 g.) was treated in ethereal solution with magnesium (1·5 g.), and after the vigorous reaction had ceased paraformaldehyde (18 g.) was added, and the whole heated for 48 hours; the product was mixed with ice and sulphuric acid, extracted with ether, the ether evaporated, the residual oil dissolved in alcohol, and the 4-methyl-α-naphthylcarbinol, m. p. 75°, obtained by fractionally precipitating the oil first with water. The carbinol was converted into *4-methyl-α-naphthylmethyl bromide* in dry benzene by means of hydrogen bromide. It crystallised from light petroleum in long needles, m. p. 77° (Found: Br, 34·3. $C_{12}H_{11}Br$ requires Br, 34·0%).

2-Methyl-α-naphthylmethyl bromide was obtained similarly

from 1-bromo-2-methylnaphthalene, and had m. p. 88° (Ziegler and Tiemann, *Ber.*, 1922, **55**, 3411).

For comparative purposes, ω-bromo-*p*-xylene was prepared from *p*-toluonitrile by reduction by Stephen's method (J., 1925, **127**, 1874) to *p*-tolualdehyde, and thence by 25% alcoholic potassium hydroxide to *p*-tolylcarbinol, which gave ω-bromo-*p*-xylene on treatment with hydrogen bromide. This should also prove a more convenient method for the preparation of the meta-isomeride than any yet published.

Attempts to prepare 4-bromo-2-methylnaphthalene were without appreciable success; the method of Vesely and Kapp (*Rec. trav. chim.*, 1925, **44**, 371) failed to produce a satisfactory yield of the required 4-amino-2-methylnaphthalene, and a method involving the bromination of aceto-2-methyl-α-naphthalide with subsequent elimination of the amino-group yielded only a trace of impure 4-bromo-2-methylnaphthalene.

Aceto-4-bromo-2-methyl-α-naphthalide.—Aceto-2-methyl-1-naphthalide (Lesser, *Annalen*, 1913, **402**, 38) (5 g.) was dissolved in 25 c.c. of glacial acetic acid, and bromine (5 g.) in glacial acetic acid (3 c.c.) slowly added. After 1 hour, the mixture was poured into water; the precipitate obtained crystallised from alcohol in flocculent needles, m. p. 223° (Found: Br, 28·7. $C_{13}H_{12}ONBr$ requires Br, 28·8%). This acetyl derivative was hydrolysed by a boiling mixture of hydrochloric acid (8 parts) and alcohol (8 parts). After 6 hours, the whole was poured into water, and concentrated ammonia added to the hot solution. The precipitated *4-bromo-2-methyl-α-naphthylamine* crystallised from light petroleum in white needles (rapidly becoming pink in the air), m. p. 82° (Found: Br, 33·4. $C_{11}H_{10}NBr$ requires Br, 33·9%); the yield was very poor.

5-Bromo-α-naphthylmethyl Bromide.—The bromination of α-naphthoic acid dissolved in warm glacial acetic acid produced 5-bromo-α-naphthoic acid, which, when recrystallised several times from alcohol, had m. p. 262° (Found: Br, 31·5. Calc.: Br, 31·8%) (Eckstrand, *J. pr. Chem.*, 1888, **38**, 155, gives m. p. 246°; Raiford and Lankelma, *J. Amer. Chem. Soc.*, 1925, **47**, 1119, give 244°). The acid was converted by means of thionyl chloride into 5-bromo-α-naphthoyl chloride (compare Raiford and Lankelma, *loc. cit.*); this was recrystallised from light petroleum (b. p. 40—60°), and reduced by Rosenmund's method (*Ber.*, 1918, **51**, 591) to 5-bromo-α-naphthaldehyde (see Rupe and Metzger, *Helv. Chim. Acta*, 1925, **8**, 838), which crystallised from light petroleum in white, prismatic needles, m. p. 104° (Found: Br, 33·9. Calc.: Br, 34·1%); *p-nitrophenylhydrazone*, red needles from acetic acid, m. p. 263°. The aldehyde was allowed to stand in contact with twice

its weight of 66% aqueous potassium hydroxide and a few drops of alcohol for 3 days, being warmed for a few minutes each day to 60°. When reduction was considered to be complete, the reaction mixture was diluted with water and extracted with ether, the extract shaken with sodium bisulphite solution to remove unchanged aldehyde, and the ether evaporated. The *5-bromo-α-naphthylcarbinol* so obtained crystallised from light petroleum as fine, white needles, m. p. 124° (Found: C, 55·5; H, 3·7. $C_{11}H_9OBr$ requires C, 55·7; H, 3·8%). Dry hydrogen bromide passed into the benzene solution of this gave *5-bromo-α-naphthylmethyl bromide*, which crystallised from light petroleum in white needles, m. p. 101° (Found: Br, hydrolysable, 26·7. $C_{11}H_8Br_2$ requires Br, hydrolysable, 26·8%).

5-Methoxy-α-naphthylmethyl Bromide.—5-Methoxy-α-naphthaldehyde (Shoesmith and Rubli, J., 1926, 3241) was prepared in a relatively large quantity (5 g.). The purification of 5-methoxy-α-naphthoic acid was more economically effected by repeated crystallisation than by our former method, and Dr. C. E. Sosson has obtained a sample of m. p. 230°. The corresponding acid chloride, obtained by the use of thionyl chloride, yields the aldehyde on reduction (yield, 30—40%).

The aldehyde was reduced as in the case of the bromo-compound above; the *5-methoxy-α-naphthylcarbinol* obtained crystallised from water in long, colourless needles, m. p. 98° (Found: C, 76·5; H, 6·3. $C_{12}H_{12}O_2$ requires C, 76·5; H, 6·4%); with dry hydrogen bromide in benzene solution it yielded *5-methoxy-α-naphthylmethyl bromide*, which crystallised from light petroleum (b. p. 40—60°) in white, prismatic needles, m. p. 65° (Found: Br, 31·4. $C_{12}H_{11}OBr$ requires Br, 31·9%). It is more stable in the air than the 4-methoxy-derivative. Both 5-bromo- and 5-methoxy-α-naphthylmethyl bromides produce a burning sensation on the skin, but neither is lachrymatory.

5-Bromo-α-naphthol.—Bromine (40 g.) was gradually dropped into vigorously stirred, *dry*, molten α-nitronaphthalene (85 g.), the temperature being maintained at 80—100°. 5-Bromo-α-nitronaphthalene, m. p. 122°, was obtained pure by crystallising the reaction mixture from alcohol, and was reduced by West's method (J., 1925, **127**, 994) to 5-bromo-α-naphthylamine, which crystallised from ligroin in plates, m. p. 69°. The insoluble sulphate of this compound was diazotised in the usual manner. The rather stable diazonium sulphate decomposed most satisfactorily when dropped into a boiling solution of 43% sulphuric acid; 5-bromo-α-naphthol was then distilled in steam, and crystallised as white needles, m. p. 137° (Fuson, *J. Amer. Chem. Soc.*, 1924, **46**, 2779).

Hydrolysis of Compounds containing Halogen in the Side Chain.—The hydrolyses were carried out at 25° in aqueous alcohol prepared by the addition of sufficient alcohol to every 10 c.c. of water to produce a volume of 100 c.c., 10 c.c. of the reagent being used for each 0·06 (approx.) g. of compound. Aliquot portions of the mixture were at intervals run into a large excess of water and rapidly titrated with standard alkali. The resulting unimolecular velocity coefficient, k (Table I), was satisfactorily constant in each case.

The rapidity of hydrolysis of 4-methyl-α-naphthylmethyl bromide (A) and 2-methyl-α-naphthylmethyl bromide (B) is seen from Table II, in which the hydrolysis of 4-bromo-α-naphthylmethyl bromide (C) is included for comparison, and t, w, and x have the same significance as in former publications.

TABLE II.

	A.	B.		C.
w =	0·5172	0·5080		0·6125
t (hours).	x.	x.	t (days).	x.
2	29	24	2	32·4
4	50	45	3	44·8
8	68	65	4	54·7
25	95	94	7	75·1

TABLE III.

Compound.	Reagent: $C_2H_4O_2$ (c.c.).	Reagent: HI (c.c.).	T.	t (hrs.).	x.
$C_{10}H_7Br(\alpha)$	10	10	100°	4	4
$C_{10}H_7Br(\beta)$	,,	,,	,,	,,	Nil
$C_{10}H_7I(\alpha)$	,,	,,	,,	,,	62
$C_{10}H_7I(\beta)$	,,	,,	,,	,,	7
$C_{10}H_7\cdot CH_2Br(\alpha)$ ...	,,	,,	,,	1	96
,, ...	,,	,,	77	2	40
,, ...	,,	,,	,,	4	65
$C_{10}H_7\cdot CH_2Br(\beta)$ ...	,,	,,	100	1	96
,, ...	,,	,,	77	2	42
,, ...	,,	,,	,,	4	71
$Br(1)\cdot C_{10}H_6\cdot OH(\beta)$	15	5	,,	0·25	94*
,,	22	,,	25	0·50	63
,,	,,	,,	,,	0·75	76
,,	,,	,,	,,	1·50	93
$Br(4)\cdot C_{10}H_6\cdot OH(\alpha)$	15	,,	77	0·25	95*
,,	22	,,	25	0·50	27
,,	,,	,,	,,	0·75	38
,,	,,	,,	,,	1·50	63
$Br(1)\cdot C_{10}H_6\cdot CH_3(\beta)$	10	,,	100	2	60
,,	,,	,,	,,	4	78
,,	,,	,,	,,	6	88
$Br(4)\cdot C_{10}H_6\cdot CH_3(\alpha)$	,,	,,	,,	2	29
,,	,,	,,	,,	4	50
,,	,,	,,	,,	6	62
$Br(5)\cdot C_{10}H_6\cdot OH(\alpha)$	,,	,,	,,	5	20

* The ease of reduction of these compounds is indicated here.

The reciprocal of the time (in days) taken for half hydrolysis of ω-bromo-*p*-xylene was 1·0.

Reduction of Various Halogenated Naphthalene Derivatives.—In Table III are summarised all the results of the reduction experiments with hydriodic acid. These were carried out in the usual manner, approximately 0·170 g. of each compound being used in glacial acetic acid and constant-boiling hydriodic acid; t and x have their usual significance, whilst T is the temperature of experiment. The liberated iodine in each case was taken as a measure of the amount of reduction which had taken place.

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CCCCIX.—*Investigation of the Constitution of Glycerides in Natural Fats. A Preliminary Outline of Two New Methods.*

By THOMAS PERCY HILDITCH and COLIN HENRY LEA.

QUANTITATIVE information in regard to the composition of the natural fats is much less available than in the case of most natural organic materials. It is only within the past few years that trustworthy data have been forthcoming as to the quantitative composition of the fatty acids present in combination in natural fats, and even at the present time the fats for which such figures are available form but a small proportion of the total number of those in common use. Information as to the manner in which these fatty acids are combined with glycerol in the natural fats is still more lacking, and it is indeed no exaggeration to say that at present we are without anything approaching quantitative knowledge of the structure of the glycerides in any of the natural fats.

The qualitative detection of individual solid glycerides by subjecting natural fats to exhaustive crystallisation from selected solvents has received much attention by several investigators, for example, Klimont (*Monatsh.*, 1902, **23**, 51; 1903, **24**, 408; 1904, **24**, 929; 1905, **26**, 563; 1912, **33**, 441; etc.), Bömer (*Z. Unters. Nahr. Genussm.*, 1907, **14**, 90; 1909, **17**, 353; 1913, **25**, 321; 1920, **40**, 97; 1924, **47**, 61; etc.) and Amberger (*ibid.*, 1913, **26**, 65; 1918, **35**, 313; 1923, **46**, 276, 291; 1924, **48**, 371; etc.); as Klimont

has emphasised, it is difficult (if not impossible) to obtain complete separation of any one component by this procedure.

The present communication is a description of the results so far obtained in some attempts to attack this complex problem by the application of new principles. We are not yet in a position to give a complete analysis of all the glycerides composing any natural fat, but there is reason to believe that further progress along the lines of investigation which we have developed will lead to more complete results in this direction. Many of the products which result from our treatment of the fats are novel in type, and new methods of separation must perforce be devised as the work develops; it is therefore probable that complete execution of the scheme we have in mind will occupy considerable time. Our procedure, however, now permits us to ascertain for the first time the proportion of completely saturated triglycerides present in a fat, and also to suggest certain general features of the structure of natural fats which have already become apparent.

General Description of the Methods employed.—The primary objective has been to alter the chemical characteristics of the glycerides in such a way that, without disturbance of the combined glyceryl radical, new glycerides may be formed which are separable more readily than the original natural mixture.

Two methods have been applied for this purpose, both of them processes of controlled oxidation which have been applied hitherto to the simple esters of the higher unsaturated fatty acids:

1. E. F. Armstrong and one of us (*J. Soc. Chem. Ind.*, 1925, **44**, 43T) showed that the methyl or ethyl ester of a higher unsaturated fatty acid, when dissolved in acetone and submitted to the action of powdered potassium permanganate, broke down almost quantitatively into a monobasic fatty acid and the hydrogen ester of a dicarboxylic acid:

$$CH_3\cdot[CH_2]_7\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2Me \longrightarrow CH_3\cdot[CH_2]_7\cdot CO_2H + HO_2C\cdot[CH_2]_7\cdot CO_2Me.$$

We have now found that the same decomposition can be effected in the case of neutral glycerides without appreciable rupture of the glyceryl ester-linking. In cases where the unsaturated glycerides are derived from either oleic, linoleic or linolenic acid, the products of oxidation are, in addition to nonoic, hexoic or propionic acid, complex glycerides united to at least one azelaic acid residue (the remaining carboxyl group of which is free). If the possible combinations of glycerol with saturated fatty acid ($S\cdot CO_2H$) and oleic acid ($U\cdot CO_2H$) be considered, it will be seen that the following products may arise:—

	Original glyceride.	Product of oxidation.
Fully saturated	$C_3H_5(O{\cdot}CO{\cdot}S)_3$	$C_3H_5(O{\cdot}CO{\cdot}S)_3$
Mono-oleo-derivative ...	$C_3H_5\begin{cases}(O{\cdot}CO{\cdot}S)_2\\(O{\cdot}CO{\cdot}U)\end{cases}$	$C_3H_5\begin{cases}(O{\cdot}CO{\cdot}S)_2\\(O{\cdot}CO{\cdot}[CH_2]_7{\cdot}CO_2H)\end{cases}$
Dioleo-derivative	$C_3H_5\begin{cases}(O{\cdot}CO{\cdot}S)\\(O{\cdot}CO{\cdot}U)_2\end{cases}$	$C_3H_5\begin{cases}(O{\cdot}CO{\cdot}S)\\(O{\cdot}CO{\cdot}[CH_2]_7{\cdot}CO_2H)_2\end{cases}$
Triolein	$C_3H_5(O{\cdot}CO{\cdot}U)_3$	$C_3H_5(O{\cdot}CO{\cdot}[CH_2]_7{\cdot}CO_2H)_3$

The acid azelaic glycerides (of which it is necessary in due course to synthesise individual representative members, in order to study and compare their characteristics) form as a rule a somewhat complicated mixture, difficult at present to separate satisfactorily. Only general discussion of these products is therefore offered at the moment, and their detailed examination is reserved for a future communication: methods for quantitative separation of the total neutral products (*i.e.*, completely saturated glycerides) from the acidic products of oxidation (emanating from any glycerides containing unsaturated fatty acids) are, however, given.

2. It was found by one of us (J., 1926, 1828) that hydrogen peroxide in concentrated acetic acid solution effected the practically complete conversion of oleic acid or of methyl oleate into a corresponding dihydroxystearic derivative. The dihydroxystearic compounds are in general distinguished from the simply fatty acids by their higher melting points and sparing solubility in most solvents, and it was thought that similar treatment of the natural fats might convert them into mixtures more amenable to fractional crystallisation than the original materials. The products to be expected may be given as follows:—

Glyceride.	Product.
Fully saturated	$C_3H_5(O{\cdot}CO{\cdot}S)_3$
Mono-oleo-derivative	$C_3H_5\begin{cases}(O{\cdot}CO{\cdot}S)_2\\(O{\cdot}CO{\cdot}[CH_2]_7{\cdot}CH(OH){\cdot}CH(OH){\cdot}[CH_2]_7{\cdot}CH_3)\end{cases}$
Dioleo-derivative	$C_3H_5\begin{cases}(O{\cdot}CO{\cdot}S)\\(O{\cdot}CO{\cdot}[CH_2]_7{\cdot}CH(OH){\cdot}CH(OH){\cdot}[CH_2]_7{\cdot}CH_3)_2\end{cases}$
Triolein	$C_3H_5(O{\cdot}CO{\cdot}[CH_2]_7{\cdot}CH(OH){\cdot}CH(OH){\cdot}[CH_2]_7{\cdot}CH_3)_3$

This method has not, up to the present, yielded results quite so promising as the more disruptive oxidation, partly in consequence of complications in the mode of addition of the hydroxyl radicals to the ethylenic linkage which escaped notice in the earlier work on the action of hydrogen peroxide upon oleic acid or its simple esters (compare Experimental, p. 3114). Nevertheless, the unsaturated glycerides can be converted completely into dihydroxylated deriv-

atives by this procedure and its employment in conjunction with the other method has assisted us in formulating the conclusions now put forward.

Discussion of the Results obtained.—We shall refer mainly in this paper to the data which we have collected on the constitution of the glycerides of mutton tallow, cacao butter, and cotton-seed oil. We hope at a later stage to report in fuller detail upon the constitution of individual fats (in addition to the above, fats such as lard, palm-kernel oil, palm oil, Chinese vegetable tallow, Illipé fat, and other vegetable and animal fats are included in the scheme of investigation by these methods in these laboratories), but we desire here to draw comparisons between different types of fat rather than to deal with individual cases.

The composition of the fatty acids combined in mutton tallow, cacao butter and cotton-seed oil is given by Armstrong and Allan (*J. Soc. Chem. Ind.*, 1924, **43**, 216T) as :

	Mutton tallow.	Cacao butter.	Cotton-seed oil.
Myristic	1·5	—	—
Palmitic	21·0	23·2	23·4
Stearic	30·0	33·6	—
Oleic	43·0	41·8	23·0
Linoleic	5·0	1·4	53·6

We may add that the fatty acids of the cacao butter used in the present experiments gave, on separation and fractional distillation of the methyl esters of the saturated and the unsaturated portions, figures in good general agreement with the above : Palmitic 24·3, stearic 34·5, oleic 39·2, linoleic 2·0.

By applying the permanganate–acetone process of oxidation to these fats, we have obtained the following figures for the percentage of completely saturated glycerides present in the original fat; the results of two separate oxidations are given in each case :

		Completely saturated glycerides, %.	Mean equivalent of fatty acids.
Mutton tallow		24·7	268·2
		26·2	266·5
Cacao butter	Below	5 *	275·4
		4·8	—
Cotton-seed oil		1·6 *	—
		1·5	—

* These figures represent maximum, rather than absolute, percentages present.

The non-volatile acidic products of oxidation, as already mentioned, are low-melting materials the complete separation of which may require considerable time; and we therefore limit discussion for the time being to the general relations disclosed between the

distribution of saturated and unsaturated fatty acids in the glycerides of vegetable and animal fats.

In mutton tallow, which contains 26% of completely saturated glycerides, the fatty acids of which have a mean equivalent of 266·5, we see that, to a first approximation, the proportions of fatty acids in the unsaturated glycerides are, by difference, about 35% of saturated and 65% of unsaturated acids.

On the other hand, the relative composition of the unsaturated glycerides of cacao butter, allowing for 5% of fully saturated glycerides (p. 3109), is about 56·5% of saturated fatty acids and 43·5% of unsaturated fatty acids.

The mean composition of the unsaturated glycerides lies in each case between that of a mono-oleic and that of a dioleic glyceride, but clearly approximates more closely to the former in cacao butter and to the latter in tallow.

So far as cacao butter is concerned, indeed, there is evidence that the predominating components are mono-oleic derivatives, and that oleopalmitostearin is an important constituent. In one of the oxidations carried out as described on p. 3112, the separation of a considerable quantity of an insoluble soap-like mass was observed at the interface between the ethereal solution and the aqueous sodium carbonate. This material was separated by filtration, washed with ether, and then acidified in the usual manner; a hard fatty substance was then obtained which possessed a saponification equivalent of 191 and an equivalent by direct titration of 703 (oleopalmitostearin requires respectively 191·5 and 766); the amount isolated in this manner (which is from the nature of the case not likely to be the whole of that present) was 60% of the total acidic glycerides produced.

The alternative method of oxidation of cacao butter in acetic acid solution with hydrogen peroxide leads to much the same conclusion. Large amounts of apparently homogeneous material, either in the form of dihydroxylated glyceride or as the monoacetyl derivative of the latter (compare p. 3114), were obtained; the products approximated in composition to glycerides containing palmitic, stearic, and dihydroxystearic acids in proportions corresponding closely with those of the palmitic, stearic, and oleic acids present in the original fat.

Whilst dioleo-derivatives are of course present to a certain extent in cacao butter, we are definitely led from our experience with both methods of oxidation to conclude that mono-oleo-derivatives predominate, and there is considerable evidence that oleopalmitostearin is an important component of the fat. This conclusion is not incompatible with Klimont's results (*loc. cit.*), but is not in

accordance with those of Amberger and Bauch (*Z. Unters. Nahr. Genussm.*, 1924, **48**, 371).*

It has been customary in some quarters to conclude that those vegetable fats (of which cacao butter is a notable example) which combine the especially useful qualities of non-greasy, brittle texture and low melting point owe these properties to the presence of certain selectively produced glycerides, and the impression is widely held that certain plants tend to elaborate specific types of glyceride. Our investigations, so far, have led to a somewhat different conclusion, namely, that the fatty acids in vegetable glycerides are distributed impartially rather than selectively, and that there is a distinct tendency towards even distribution of unsaturated acids throughout the whole fat, so that the occurrence of simple triglycerides, and even of mixed saturated glycerides, is reduced to a minimum. If this be the case, the physical properties of a mature vegetable fat depend primarily upon the mixture of fatty acids from which it emanates.

Hence, in the case of cacao butter, in which the proportions of palmitic, stearic and oleic acids approach equality relatively more closely than in most fats, it is not unnatural that the final mixture resembles an individual glyceride in properties more nearly than a fat in which the variation in kind and proportion of the component fatty acids is more pronounced.

Again, permanganate–acetone oxidation of cotton-seed oil has proved that entirely saturated glycerides are present only in very small proportion, although 25% of the combined fatty acids is palmitic acid; this acid is thus practically wholly in combination as mixed glycerides with the unsaturated fatty acids, which in this oil are present in the proportion of about three molecules per molecule of palmitic acid.

Also, work on palm-kernel oil, at present in an early stage in these laboratories, has already indicated that the oleic acid present is combined almost entirely with saturated fatty acids in mono- or di-oleic glycerides.

The only animal fat yet studied by these methods, mutton tallow, has yielded data which point to an entirely different state of affairs, the amount of fully saturated glycerides present being far larger than that in the vegetable fats. We prefer, naturally, to defer further discussion of the animal fats until we have collected a wider range of analytical data.

* These authors state that cacao butter contains 55% of palmitodiolein, 25% of oleodistearin, and 20% of oleopalmitostearin; the calculated iodine value of the original fat is thus 45·7, whereas the recorded figure is 38·6.

Experimental.

I. *Oxidation of Glycerides with Potassium Permanganate in Acetone Solution.*—The fats employed were of best edible quality and were submitted to oxidation in the neutral condition, *i.e.*, after removal of free fatty acids by washing with dilute aqueous alkali.

The procedure employed in working up the products of oxidation differed somewhat in detail with the various fats oxidised, but a typical experiment with mutton tallow may be described.

Mutton tallow. The tallow (100 g.) was dissolved in anhydrous acetone (1000 c.c.), and powdered potassium permanganate (250 g.) added in small quantities with frequent shaking; the heat of reaction was sufficient to keep the acetone in vigorous ebullition (reflux condenser). The mixture was refluxed for 4 hours and kept overnight. (The admixture of sufficient anhydrous magnesium sulphate with the permanganate to neutralise potassium hydroxide liberated during oxidation is a further precaution which we have employed in some cases in order to restrain any tendency to glyceride saponification.) The acetone was distilled off and the residue after admixture with water was treated with sodium hydrogen sulphite and 30% sulphuric acid (the slightest possible excess of free sulphuric acid being maintained) at a moderate temperature until decolorised. The product was extracted several times with somewhat large quantities of ether. In the particular experiment described, the first ethereal extract deposited on standing a white, crystalline solid, which was recrystallised from acetone (A). The combined ethereal extracts were washed free from mineral acid, evaporated to dryness, and combined with the residue from the acetone mother-liquor of (A). This product was dissolved in a little hot alcohol and titrated against *N*-alcoholic potash; the neutralised solution was now poured into aqueous sodium carbonate and extracted repeatedly with ether to remove neutral matter.

The acidic glyceride products of oxidation are not removed efficiently by simple agitation of the ethereal solution with aqueous sodium carbonate, and as an alternative to the potash neutralisation process outlined above, the following method has been used, particularly when the proportion of fully saturated glyceride in the original fat is fairly large (as in mutton tallow and palm-kernel oil).

The crude oxidation product is boiled with a slight excess of sodium carbonate until a clear layer of neutral fat separates on the surface. The aqueous layer, still retaining a considerable amount of emulsified neutral fat, is syphoned off, and the separated neutral product washed by boiling with water until free from alkali. The united alkali extract and washings are now repeatedly extracted with ether as above.

By these methods a separation is ultimately achieved yielding on the one hand the acidic products of oxidation substantially free from neutral glycerides and on the other the neutral product containing only traces of acid substances. Thus in the experiment cited above, the following results were obtained:

A. White solid separated from ether and acetone—completely neutral, 12·5 g.

B. "Neutral" residue from ether, still containing a little soap, 24 g.

C. Acidic glycerides recovered from alkali solutions: partly freed from monobasic (nonoic) acids produced in the oxidation by heating at 95—100°/2 mm. until the weight became constant. Not submitted to further oxidation, 66·4 g.

B possessed an iodine number of 7·5 (original tallow, iodine number 41·2) and was reoxidised with 4 times its weight of powdered permanganate in acetone solution; the products were worked up by a combination of the methods described above, yielding 15·3 g. of neutral products (D) and 5·1 g. of acidic products (E).

Thus there were obtained in all 27·8 g. of crude neutral glyceride (A and D) and 71·5 g. of acidic glyceride (C and E).

The crude neutral glyceride (27·8 g.) was finally purified by boiling with dilute sodium carbonate solution and then repeatedly with water, the aqueous and alkaline liquors being then united as before and exhaustively extracted with ether. There was thus obtained a total proportion of 26·4% of fully saturated glycerides in the original tallow.

The fully saturated glyceride—iodine number 0·8—gave on saponification a mixture of fatty acids the mean equivalent of which was 266·5, corresponding to 59·8% of palmitic and 40·2% of stearic acid.

In another independent oxidation of mutton tallow, the fully saturated glycerides were 24·7% of the total fat—the fatty acids having a mean equivalent of 268·2.

Cacao butter. Two similar oxidations of cacao butter were undertaken with the following results:

		Expt. I.	Expt. II.	Calc.*
First oxidation	neutral product	22·1	24·7	
	iodine number	6·5	8·9	
Re-oxidation of neutral product	fully-saturated glycerides	4·8	4·8	
	iodine number	1·6	1·1	
	mean equivalent of combined fatty acids	275·4		
Combined acidic products (free from monobasic acids)		79	79·5	81·9
Mean saponification equivalent		174·0	174·4	174·7

* On the basis of 5% and 1·5% of saturated glycerides respectively.

Cotton-seed oil. The final general results obtained so far are :

	Expt. I.	Expt. II.	Calc.*
Fully saturated glycerides	1·6	1·5	
Combined acidic products (free from monobasic acids)	(80) †	68·3	73·4
Mean saponification equivalent		123·1	123·2
Combined acidic products (solids insoluble in cold ethyl acetate)	53·6		
Mean equivalent	137·6		

* On the basis of 5% and 1·5% of saturated glycerides respectively.
† Not freed from nonoic acid.

II. *Oxidation of Glycerides with Concentrated Hydrogen Peroxide and Acetic Acid.*—Neutral unsaturated fats are oxidised with much the same ease as the corresponding fatty acids or methyl esters when agitated at 40—80° with excess of concentrated hydrogen peroxide in moderately concentrated acetic acid solution. The products contain, however, not only glycerides of dihydroxystearic acid, but also a considerable proportion of the latter in the monoacetylated form. The presence of combined acetic acid in these compounds was apparent at an early stage of the investigations and, whilst at first it seemed possible that displacement of one or other higher fatty acid radical by that of acetic acid had occurred, we were able to satisfy ourselves that this took place, if at all, only to an insignificant extent, and that the quantitative data at our disposal definitely pointed to acetylation of one of the hydroxyl groups introduced.

The conditions employed in earlier work by one of us (Hilditch, J., 1926, 1828) on the oxidation of methyl oleate or oleic acid by this reagent probably led to the presence of any monoacetyl derivatives of dihydroxystearic acid or its methyl ester being overlooked, and we hope shortly to return to the study of this action in its simpler applications in the light of the present results.

In the meantime the presence of a considerable degree of acetylation in the products from hydrogen peroxide oxidation of the neutral glycerides has unfortunately complicated matters seriously, since it is obviously very difficult (although apparently not impossible) to remove the acetyl residues without at the same time hydrolysing the glycerides themselves. It is possible to reduce the amount of acetylation to some extent by conducting the process in more dilute acetic acid and at as low a temperature as possible (40—50°), but the oxidation then becomes very slow and is difficult to carry to completion even after several days. We consider at

present that the more promising procedure is to operate in concentrated acetic acid solution at a fairly high temperature; the oxidation then proceeds rapidly to completion. A description will be given of preliminary results obtained in this way with cacao butter and mutton tallow.

Cacao butter. Cacao butter (100 g.) was heated with glacial acetic acid (400 c.c.) in a wide-necked conical flask provided with a good mechanical stirrer and immersed in a water-bath maintained at 75—80°. 35% Hydrogen peroxide solution (50 c.c.) was added, further additions of 25 c.c. of this solution being made after 2 hours and after 5 hours from the commencement. After a total period of 9 hours at 75—80° with constant stirring, the product was cooled and poured into water. A large quantity of hard, tough solid separated and was removed, and the filtrate was made alkaline with excess of sodium carbonate solution and then extracted with ether several times. The solid cake was dissolved in the ethereal solution, and the whole washed with water.

The residual fat from the washed ethereal extract was boiled in water with a slight excess of dilute sodium carbonate solution, settled, and separated from the aqueous layer by siphoning off the latter, and then washed similarly and repeatedly with boiling water until neutral. The aqueous and alkaline washings were united and re-extracted with ether. There were thus obtained 101·6 g. of neutral product (95·8 g. from the aqueous extraction, and 5·8 g. recovered by ether from the aqueous layers).

All aqueous and alkaline liquors were methodically acidified and the higher fatty acids (4·3 g.) recovered.

The neutral product (101·6 g.) had an iodine number of 1·6 and a saponification equivalent of 251·5 (calc. from the known composition of the total fatty acids, 302·9 as dihydroxystearic derivative, or 225·3 if the latter are in the monoacetylated form); it contained 3·0% of combined acetic acid (as $CH_3 \cdot CO$).

From the mean equivalent (251·5) of this product, it may be calculated that (*a*) assuming displacement of fatty acid by acetic acid in the glyceride itself, the fatty acids displaced should have amounted to 22·4 g. of the total product, with production of 86·8 g. of neutral product; (*b*) assuming acetylation of the dihydroxystearic radical produced, there should have been no production of free fatty acids and a yield of 108·5 g. of neutral product.

The experimental data are thus strongly in favour of the latter hypothesis, the small amount of free fatty acid observed being accountable for by slight hydrolysis under the conditions of the reaction.

The neutral product was resolved by repeated systematic fractional crystallisation from acetone into the following fractions:

		% of whole.	Sap. eq.
A.	Least soluble; apparently homogeneous, hard, white, crystalline solid, m. p. 68—69°	22·5	293·4
B.	Sparingly soluble; hard and crystalline; gelatinises with acetone; m. p. 47°	6	256·6
C.	Intermediate fraction; soft, granular mass, m. p. 38—42° (indef.)	4	243·3
D.	From combined mother-liquors (except the first); soft, oily paste	42·5	241·1
E.	Most soluble portion from first crystallisation; oily	25	231·7

Dihydroxystearic acid (m. p. 95°) was present as glyceride in all these fractions, but a rigid method for its separate determination when mixed with palmitic and stearic acids is not yet available.

The mixed acids (mean equivalent 284·5) from fraction A, however, yielded by crystallisation from light petroleum 77% of the amount of this acid which would be required for the product derived from an original mono-oleic glyceride. This fraction apparently still contained traces of acetylated products.

Fractions D and E contained considerable quantities of acetylated products [CH_3·CO found: 3·45% (D) and 4·35% (E)].

These results indicate that the hydrogen peroxide treatment of unsaturated glycerides leads to a complicated mixture of products and that the method in its present stage of development is not adapted for quantitative work; nevertheless the above group of fractions affords confirmatory evidence of the general and to a large extent even distribution of oleic acid throughout the glycerides present in cacao butter.

Mutton tallow. Mutton tallow (100 g.) was oxidised in acetic acid with 35% hydrogen peroxide solution under exactly the same conditions as cacao butter. After 9 hours' treatment at 75—80° the mixture was cooled, and the neutral portion of the product obtained free from acetic acid and traces of fatty acid.

The neutral product (100·7 g.) had an iodine number of 1·6 and a saponification equivalent of 245·3; it contained 4·65% of acetic acid (calculated as CH_3·CO). The yield of neutral product, together with its content of combined acetic acid, points, as in the previous case, to acetylation of one of the hydroxyl groups rather than to displacement of fatty acid residues by acetic acid in the glycerides present.

The product was similar in general appearance to that from cacao butter and was separable by crystallisation from acetone into a hard, white, sparingly soluble material and more soluble constituents. Quantitative resolution of the hydroxylated tallow by

this means is at present in progress and the results will form part of a subsequent communication.

We wish to acknowledge the assistance of Mr. G. Collin (who is also engaged in the investigation of palm-kernel oil by these methods) in connexion with one of the oxidations of cotton-seed oil referred to in this paper.

THE UNIVERSITY, LIVERPOOL. [*Received, October 25th*, 1927.]

CCCCX.—*The Heat of Adsorption of Oxygen on Charcoal.*

By ANGUS FITZCHARLES HENDERSON WARD and ERIC KEIGHTLEY RIDEAL.

CALORIMETRIC determinations of the heat evolution on adsorption of oxygen by charcoal have been made by Dewar (*Proc. Roy. Soc.*, 1904, *A*, **122**, 1904), Blench and Garner (J., 1924, **125**, 1288), and Keyes and Marshall (*J. Amer. Chem. Soc.*, 1927, **49**, 156). In extending Warburg's work (*Biochem. Z.*, 1924, **145**, 461) on oxidation at charcoal surfaces, Rideal and Wright (J., 1925, **127**, 1347) and Wright (this vol., p. 2323) showed that in a sugar charcoal three different types of surface could be distinguished and their relative areas determined by the method of selective poisoning. The most active area permits autoxidation when the charcoal is shaken with water containing dissolved air or oxygen. The reaction is of zero order, due to the escape of carbon dioxide from the active patches. It is natural to suspect that the portions of the charcoal surface which, according to these observations, are readily autoxidisable would be those on which the energy change, as noted in the calorimetric experiments of Blench and Garner on adsorption of the gas, would likewise be greatest.

Since charcoal is an extremely variable material, and different results are obtained from samples prepared in different ways, it seemed desirable to use several varieties and to attempt to correlate the heats of adsorption of oxygen with other properties of the charcoal. The determination of the heats of adsorption for four different charcoals is now described, together with the rate of autoxidation, the true densities, the apparent bulk densities, the adsorption of methylene-blue at p_H 6·5, and the particle size.

EXPERIMENTAL.

The charcoals employed were: (1) Merck's blood charcoal, purified by digestion with hydrochloric acid and activated by

heating in air for ½ hour to dull redness; (2) Griffin's sugar charcoal, reignited and washed; (3) "supra-norite," made from wood dry distilled at 700° and then activated by superheated steam; (4) potash sugar charcoal, prepared by charring lump sugar with 20% of potassium carbonate in a porcelain dish and extracting the mass with hydrochloric acid, and, after prolonged reflux washing with boiling water, activated by ignition in a silver crucible. We are indebted to Dr. C. G. L. Wolf for the last three charcoals.

Determination of the Adsorption of Methylene-blue.—The adsorption isotherms of charcoal for various solutes vary greatly. With iodine or acetic acid, the amount adsorbed is proportional to the bulk concentration over a wide range; but phenol, quinine, and methylene-blue reach adsorption maxima at low concentrations (Honig, *Koll.-Chem. Beih.*, 1926, **22**, 345). Kruyt, Pincussen, and Warburg have offered various objections to the use of methylene-blue, but Paneth and Radu (*Ber.*, 1924, **57**, 1221), from experiments on powdered diamond and charcoal, conclude that the saturation maximum is attained on covering the available surface with a unimolecular layer of the dye. Methylene-blue will, however, give no indication of the extent of the micro-pores owing to the size of the molecule; for example, active coconut charcoal readily adsorbs gases and acetone, but its methylene-blue adsorption is small. The adsorption of many dyes varies with the acidity of the solution, and all determinations were conducted at p_H 6·5. A solution of methylene-blue containing 1 mg. per c.c. was added to 0·1 g. of charcoal (more in the case of sugar charcoal) from a burette until it ceased to be completely decolorised on shaking and keeping for some while. Further quantities of the dye were then added and the residual amounts in the solution were determined colorimetrically with the aid of a Klett biocolorimeter. The results, obtained on the assumptions of Paneth and Radu, that 1 mg. of dye will cover 1 sq. m. of surface, are as follows:

Charcoal.	Areas (sq. m. per g.).	Mean.
(1)	642, 644, 573, 630	622
(2)	8·4 7·5	8·0
(3)	503 546	525
(4)	6·0 5·0	5·5

The ash contents of the dried charcoals, determined by the slow ignition of about 0·5 g. and heating the residue until of constant weight, were:

Charcoal	(1)	(2)	(3)	(4)
Ash content, %	1·00	0·15	9·59	0·37

The densities of the charcoals were determined by opening specimens of charcoal sealed in glass under water after prior exhaustion with a

diffusion pump for 5 hours, the charcoals having been heated at 200° to 300° during the process of exhaustion. In such determinations there occurs a " drift " in the values obtained for the densities (Cude and Hulett, *J. Amer. Chem. Soc.*, 1920, **42**, 391), due to the gradual penetration of the liquid into the micro-pores. The values obtained after 15 minutes' immersion are found to differ from the " infinity " value by about one unit in the third decimal place. This period was accordingly adopted as convenient for these experiments. The apparent bulk densities, which gave an indication of the state of aggregation, were determined by weighing the amount of the powders necessary to fill a definite volume, the tubes being tapped to ensure uniformity of packing. The values obtained were reproducible. The charcoals were also examined for possible changes in the apparent bulk densities after the experiments on the adsorption of oxygen had been completed. The results obtained are in the following tables :

		Apparent bulk density	
Charcoal.	True density.	(before).	(after).
(1)	1·37	0·22	0·22
(2)	1·42	0·58	0·58
(3)	2·03	0·14	0·115
(4)	1·43	0·30	0·32

It will be noted that charcoal (3) is relatively unstable, in that the apparent bulk density undergoes a diminution during the process of exhaustion necessary for the determination of the heat of adsorption of oxygen, although the charcoal did not lose weight to any measurable extent during evacuation. This charcoal has a true density of above 2·0, yet its bulk density is least, an indication that the ash of the charcoal probably gives a support to enable the charcoal to exist in a much more porous but unstable state.

The rates of autoxidation of the charcoals were determined at 40° with the aid of a Barcroft differential shaking machine in the manner described by Rideal and Wright (J., 1925, **127**, 1347), and are given for specimens of the charcoal both before and after the determination of the heats of adsorption of oxygen :

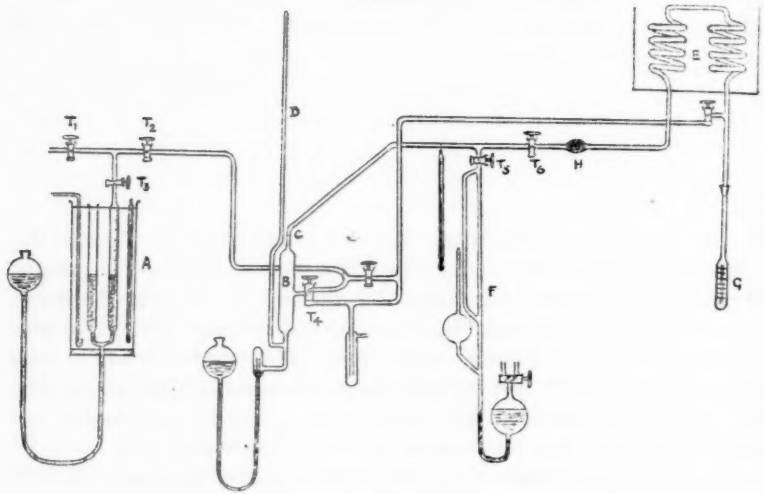
Rate of autoxidation (in mm.^{3} of O_2 at *N.T.P.* per g. per hour at 40°).

	Before adsorption experiments.			After adsorption experiments.		
Charcoal.			Mean.			Mean.
(1)	232	229	230	242	244	243
(2)	165	159	162	196	208	202
(3)	64·8	72·8	69	218	209	214
(4)	352	364	358	316	318	317

Again it will be noted that charcoal (3) is exceptional, in that the process of prolonged exhaustion necessary for the determination of the heat of adsorption has caused a very considerable increase in the autoxidisable area.

The Determination of Particle Size.—The sizes of the charcoal particles were measured with the microscope and oil-immersion objective, with a scale in the eye-piece. This was standardised by comparison with blood corpuscles (7μ diameter). Charcoals (2), (3), and (4) were fairly homogeneous, but (1) varied considerably, the largest particles being seven or eight times the smallest. For (2), (3), and (4), the maximum variation in size was 3- or 4-fold. Charcoal (1) was made up of particles of very irregular shape, charcoals (2) and (4) were almost cubic or spherical, and in charcoal (3) one-third of its particles consisted of thin rods, with a length of five or six times the thickness. The diameter given below represents for this charcoal an average value of the different dimensions. The

FIG. 1.



mean diameters of the charcoals are as follows (average of measurements on a large number of particles):

(1) 8·1μ; (2) 5·8μ; (3) 4·9μ; (4) 5·8μ.

Brownian movements were easily observed in the case of the smallest particles.

Determination of the Adsorption and Heats of Adsorption of Oxygen.—The oxygen was prepared by the electrolysis of a 10% solution of caustic soda, and passed over calcium chloride, solid potash, and phosphoric anhydride; in order to remove any hydrogen present the gas was then passed over palladium-asbestos, and again dried by phosphoric anhydride. The oxygen was introduced into the measuring burette A (Fig. 1), which was enclosed in a water jacket

kept at uniform temperature by a fine stream of air bubbles being driven through it.

In an experiment, the taps T_2 and T_3 were kept open, and a measured quantity of the gas was delivered into the vessel B by way of the three-way tap T_4. This was a hollow-barrel tap by which B could be put into communication with either the burette or the high-vacuum pumps (a Langmuir pattern mercury-vapour diffusion pump, backed by a Hyvac pump). The vacuum kept the barrel well pressed down all the time. By raising the level of the mercury in B to the mark C, the gas could be driven over *via* the tap T_6 and the spirals of capillary tubing E (kept in melting ice) into the adsorption vessel G. This was made of Pyrex glass and connected to the rest of the apparatus by a ground joint. Inside G was placed a thin rod of Pyrex with several discs on it, to keep the charcoal from being pressed down too tightly. The possible poisoning of the charcoal by mercury vapour was prevented by a small tube containing gold foil (H in the figure). The pressure of the oxygen was measured on the tube and scale D.

For the measurement of the heat of adsorption, the Bunsen ice calorimeter was used, as described by Schüller and Wartha (*Wied. Ann.*, 1877, **1**, 359). Instead, however, of their method of weighing the mercury which moved along the capillary tube, it was found sufficiently accurate, and much quicker, to measure the distance that the mercury meniscus moved along the tube by means of a scale behind. The inner tube of the calorimeter was about half filled with mercury to ensure good contact with the source of heat placed inside it. The calibration of the instrument was effected by introducing weighed amounts of various metals at known temperatures and with known specific heats, and the movement of the mercury along the scale was observed. After various methods of freezing a sheath of ice round the central tube had been tried, it was found that the most convenient method was to push down the centre an iron rod which had been cooled in liquid air. The mercury caused uniform cooling, and the ice sheath was regular.

Since the water inside the calorimeter is under a slight pressure due to the column of mercury, Lamb and Coolidge (*J. Amer. Chem. Soc.*, 1920, **42**, 1146) put a couple of drops of alcohol in the water of the surrounding vessel to depress its freezing point by the same amount and prevent the gradual movement of the mercury meniscus due to the slow melting of the ice sheath. In these experiments it was found that this effect was altogether masked by the impurity of the ice in the outer jacket, which was at a slightly lower temperature than 0°, and caused a slow freezing inside. This was decreased by first washing the ice in distilled water, but could not

be got rid of entirely; this, however, proved to be no disadvantage, for by the method adopted readings could be taken more quickly when there was a slight outward movement of the mercury.

At the beginning of an experiment, a weighed quantity of charcoal was placed in the adsorption vessel, and baked for 2 or 3 days at about 420° until the pressure decreased to about 10^{-5} mm. At the beginning of the evacuation there was always a danger of some of the charcoal being carried away owing to the rapidity of evolution of gas. To prevent this a small wad of cotton wool was placed in the tube leading out of the adsorption vessel.

When the pressure was sufficiently low, the tap T_5 was closed, and the McLeod gauge shut off from the rest of the apparatus. The ice calorimeter was then placed under the adsorption vessel and raised into position. After equilibrium had been reached (about 2 hours), a small amount of gas was transferred from the burette A into B, and then driven into the vessel C. The pressure of the oxygen, as measured on the scale D, gradually decreased as more of the gas was adsorbed, and at the end of about $\frac{1}{4}$ hour had reached its final value. More gas was then transferred from the burette, and the procedure repeated. At each reading of the pressure or volume, the temperature of the air in the neighbourhood of the apparatus and that of the water jacket round the burette were observed.

The volume of the adsorption vessel and the tubes leading to it, as far as the mark C, had previously been determined by letting in various known amounts of gas and measuring the pressure. In an actual adsorption experiment, part of the volume of the system is at room temperature, and part at 0°. The volume of the part at room temperature was found by measuring the lengths and internal diameters of the various tubes that made it up, and by subtracting this from the total volume, the volume of the part at 0° was found. The relative amounts of these two volumes need not be known so accurately as the total volume, as the error due to this is not so great.

The amount of gas adsorbed was determined as follows.

Let v_1 = volume of system at room temperature; v_2 = volume of system at 0° (allowance must be made here for the volume actually occupied by the charcoal); P = atmospheric pressure; p = pressure of gas in the system; t = room temperature; T = temperature of burette; and V = volume of gas from burette. Then if the volume of V corrected to *N.T.P.* is V',

$$V' = 273VP/760(273 + T).$$

If the volume of gas which fills v_1 becomes v_1' when reduced to *N.T.P.*, then

$$v_1' = 273v_1p/760(273 + t);$$

v_2' similarly defined would then be given by $v_2' = pv_2/760$, and the amount of gas adsorbed (in c.c. at *N.T.P.*) would be $V' - (v_1' + v_2')$. From this the amount adsorbed per g. is easily found. The results obtained with the various charcoals are given graphically, the amount of oxygen adsorbed being plotted against the pressure.

With the calorimeter in position scale readings were taken at frequent intervals and plotted against time on as large a scale as possible. In the intervals between the liberations of heat, parallel straight lines were obtained, but when the gas was let in there was a resulting inflexion in the curve, which again became straight when equilibrium was reached. The distance between the lines, measured parallel to the axis of scale readings, was proportional to the heat evolved. With the capillary tube used, the sensitivity of the instrument was about 0·5 cal. per mm. of the scale. The sensitivity of the calorimeter depends, of course, on the diameter of the capillary tube, but it is not convenient to use capillary tubes narrower than this, as the mercury sticks and makes accurate reading difficult.

By this means the evolution of heat was found for each small addition of gas, and after summing these, a curve was plotted for the total amount of heat liberated against the total amount of gas adsorbed at different pressures (integral heat of adsorption). The slope of the tangent to the curve at any point gave the differential heat of adsorption in cals. per c.c. or cals. per g.-mol. according to the scale used. These values were then plotted against the amount of gas adsorbed.

Results.

Table I is an example of the experimental results [for the charcoal (1)]. For the other charcoals similar results were obtained, but these are only shown graphically.

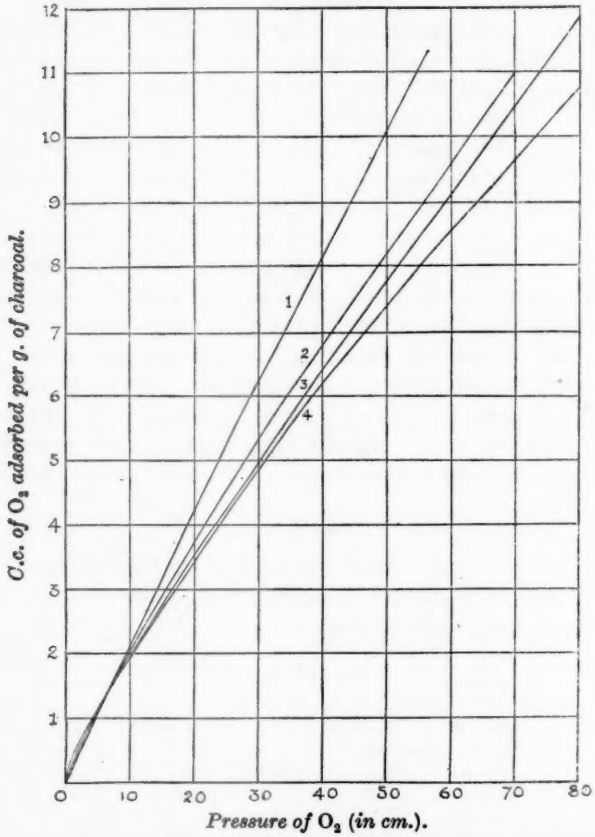
TABLE I.

Expt.	Press. of O_2 (cm.).	C.c. O_2 adsorbed per g.	Sum of differential heats (cals. per g.).
(1) 1	11·20	2·35	0·96
	26·10	5·28	1·53
	40·75	8·05	2·30
(1) 2	13·20	2·90	1·62
	20·50	4·38	1·97
	38·48	8·02	2·74
	49·21	10·05	3·30
	71·71	14·08	4·03
(1) 3	1·00	0·21	0·38
	3·30	0·72	0·76
	5·87	1·38	0·92
(1) 3	10·85	2·38	1·20
	23·85	5·06	1·66
	35·47	7·37	2·14
	50·80	10·37	2·64
	62·70	12·42	3·11
(1) 4	1·52	0·28	0·48
	3·15	0·65	0·71
	8·00	1·77	1·01
	20·53	4·54	1·39
	55·40	11·22	2·54
	70·30	13·82	3·07

The amounts of oxygen adsorbed at different pressures are shown on the adsorption isotherms (Fig. 2). For any particular

charcoal, the figures found in the different runs fall very closely on the same curve. There is not much difference in the curves for the different charcoals, (2), (3), and (4) being almost identical, and (1) slightly greater. The isotherms, although not quite straight lines, are nevertheless very far from the shape to be expected if the adsorption maximum were almost reached. They are very nearly

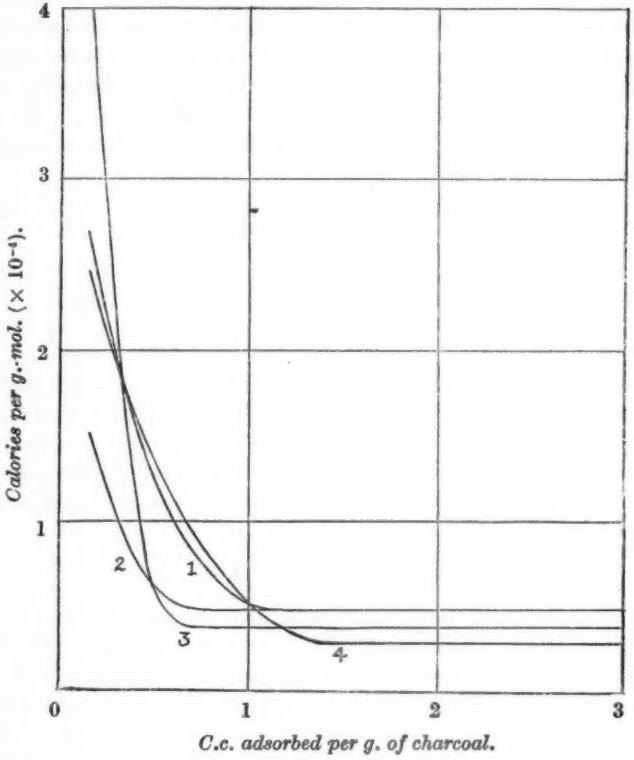
FIG. 2.



linear at the beginning of the curve, when the amount adsorbed is almost directly proportional to the pressure. Just by the origin, however, there is a slight divergence from this, especially noticeable for the charcoal (4). The curve, which is nearly straight down to about 4 cm., bends downwards and becomes slightly concave to the pressure axis; *i.e.*, at low pressures the charcoal adsorbs rather more oxygen for a given pressure increase than at higher concentrations. This effect occurs also with (2) and (3) although to a less extent.

More marked differences in behaviour between the charcoals are found when the heat of adsorption of oxygen (in cals. per g.-mol.; mean of several experiments) is plotted against the amount adsorbed, Fig. 3. For one charcoal, the agreement in this case between different runs is not nearly so good as for the adsorption isotherm. This is not due to inaccuracies of measurement, for the divergencies obtained are much greater than the possible error of the ice calori-

FIG. 3.



meter. The charcoal surface must have been altered in some way during the out-gassing between runs. As far as possible, the same temperature was used in all cases, but owing to difficulties of control, an error of 10° in the regulation was not impossible; moreover, owing to various circumstances, the out-gassing was continued for different times (1, 2, or 3 days).

The first noteworthy point about the heat evolution curves is the initial steep part, owing to the relatively high heat of adsorption for the first amount of oxygen adsorbed. On account of the small

capacity of the calorimeter system it was found impracticable to work with more than 1·5 g. of charcoal; in addition, the sensitivity was such that accurate measurements both of the amounts of oxygen adsorbed and of the corresponding thermal evolution could not be conducted on less than 0·15 c.c. adsorbed per g. With these quantities, the ascending portions of the Q,x curve noted by Garner would not be obtained, but the relatively high heats of adsorption for the initial steep portions of the curve could be accurately determined. In the graphs, the straight portions of the curve indicate uniformity of properties and a constant heat of adsorption, but the portions near the origin correspond to the areas of the charcoal more active in adsorption. From a determination of the area covered by this amount of oxygen, the area of the active patches can readily be found. The volumes of oxygen adsorbed with an increased heat evolution are approximately as follows:

Charcoal	(1)	(2)	(3)	(4)
C.c. strongly adsorbed (per g. at *N.T.P.*)	1·0	0·6	0·6	1·3

Taking the radius of the oxygen molecule as 1·81 Å. (Jeans, "Dynamical Theory of Gases"), we obtain for the respective areas

(1) 2·78 m.^{2}; (2) 1·67 m.^{2}; (3) 1·67 m.^{2}; (4) 3·62 m.^{2}.

These areas vary in the same order as do the rates of autoxidation of the charcoals. Neglecting charcoal (3), which we have noted as being extremely variable in nature and possessing a very high initial heat of adsorption for oxygen, we obtain the following ratios between the areas of the active portions and the rates of autoxidation.

(1) $2{\cdot}78/230 = 0{\cdot}0121$; (2) $1{\cdot}67/162 = 0{\cdot}0103$;
(4) $3{\cdot}62/358 = 0{\cdot}0101$.

This agreement is as satisfactory as could be expected in view of the inaccuracies in estimating the areas of the patches with high heats of adsorption. A further comparison may be made with the data on selective poisoning furnished by the experiments of Rideal and Wright (*loc. cit.*). In their experiments, it was found that poisoning of the autoxidation of a charcoal, which consumed oxygen at the rate of 0·013 mm.^{3} per mg. per hour at 40°, was effected on adsorption of $2{\cdot}38 \times 10^{15}$ molecules of amyl alcohol per mg.

With this value, and since poisoning of autoxidation appears to be a linear function of the amount adsorbed, it is possible to calculate the number of molecules of amyl alcohol which would be necessary to poison these much more active charcoals, and to compare these values, derived from entirely different charcoals and by a different method, with the quantities of oxygen adsorbed on the active areas. These data are in the following table:

Charcoal.	Rate of autoxidation (mm.^{3} per g. per hr. at 40°).	No. molecules amyl alcohol ($\times 10^{-19}$) per g. required to poison.	C.c. of O_2 adsorbed per g. with high heat of adsorption.	Equiv. no. of molecules ($\times 10^{-19}$) adsorbed per g.	Ratio, Col. 3 / Col. 5
(1)	230	4·22	1·0	2·70	1·56
(2)	162	2·96	0·6	1·62	1·83
(3)	67	1·22	0·6	1·62	0·75
(4)	358	6·56	1·3	3·52	1·86

On comparison of the data in cols. 3 and 5 for the charcoals (1), (2), and (4), it is clear that the method of poisoning with amyl alcohol and the thermal method for oxygen adsorption yield results for the extent of the autoxidisable areas of charcoals in close agreement with one another. It cannot, of course, be definitely stated that all the oxygen molecules adsorbed with a heat evolution in excess of the normal relate to the autoxidisable portion, or that the ratios in col. 6 bear any relationship to the relative covering powers of amyl alcohol and oxygen molecules on the charcoal surfaces, for there is no reason to suppose that the selectiveness of the adsorptions on the active portions of the charcoal surfaces is identical for each material. It is interesting to note that these ratios are consistent for the three stable charcoals when it is assumed that all the oxygen adsorbed with a high heat evolution is autoxidisable: if the assumption is restricted to the quantity of oxygen adsorbed with heat evolutions exceeding 10,000 (or 20,000) cals. per g.-mol., then the ratio between this quantity and the rate of autoxidation shows rapidly increasing discrepancies between the different charcoals.

Finally, Keyes and Marshall supposed that the high initial heat corresponded to the first unimolecular layer, and that the lower subsequent heats were due to the building up of thicker films of adsorbed oxygen, but as a result of our work their view seems improbable for the following reasons: The fact that the adsorption isotherm is nearly a straight line means that the charcoal is not nearly saturated; and also, to take the case of charcoal (1) which is most adsorbent, even at atmospheric pressure the oxygen only covers 1/50 of the methylene-blue area, and, on account of the large size of the molecule of the dye, this is a considerable under-estimate of the total area available for the oxygen.

Summary.

1. Experiments have been conducted on four different types of charcoal and the following properties investigated: the adsorption of oxygen and the heat of adsorption, the rate of autoxidation, the area of methylene-blue adsorption, the ash content, the true and the apparent bulk densities, and the particle size.

2. The high initial heats of adsorption have been determined and

the areas of the corresponding active patches have been found to be proportional to the rates of autoxidation of the charcoals.

3. The covering power of oxygen has been compared with that of amyl alcohol and shown to be of the same order and to have a constant ratio for all charcoals.

4. In the case of a charcoal with a high ash content, an instability of the carbon surface and a very high initial heat of adsorption for oxygen were found.

Our thanks are given to Jesus College for the provision of a Scholarship, and to the Department of Scientific and Industrial Research for a research grant to one of us (A. F. H. W.) which permitted this investigation to be carried out.

LABORATORY OF PHYSICAL CHEMISTRY,
CAMBRIDGE. [*Received, November 3rd,* 1927.]

CCCCXI.—*The Condensation of Glyoxalines with Formaldehyde.*

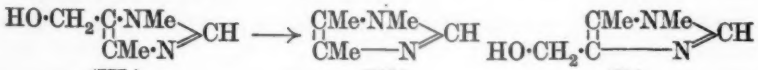
By ROBERT GRINDLEY and FRANK LEE PYMAN.

FEW examples of the condensation of glyoxalines with aldehydes have been studied hitherto. Windaus (*Ber.*, 1909, **42**, 758) has shown that the condensation product of 4(5)-methylglyoxaline and formaldehyde is 4(5)-methyl-5(4)-hydroxymethylglyoxaline, since it gave 4 : 5-dimethylglyoxaline on reduction, and Ewins (J., 1911, **99**, 2052) isolated the condensation product in a yield of 43%. Chloral also substitutes 4(5)-methylglyoxaline in the 5(4)-position (Gerngross, *Ber.*, 1912, **45**, 509), whilst both histidine (Wellisch, *Biochem. Z.*, 1913, **49**, 173) and histamine (Fränkel and Zeimer, *ibid.*, 1920, **110**, 234) yield dicyclic compounds on condensation with methylal and hydrochloric acid, the glyoxaline ring being here also substituted in the 5(4)-position. On the other hand, 5-chloro-1-methylglyoxaline condenses with formaldehyde to give 5-chloro-1-methyl-2-hydroxymethylglyoxaline in good yield (Sarasin, *Helv. Chim. Acta*, 1923, **6**, 377; 1924, **7**, 713; Sonn, Hotes, and Sieg, *Ber.*, 1924, **57**, 953, 2134) and 5-bromo-1-methylglyoxaline similarly yields a 2-hydroxymethyl derivative (Balaban and Pyman, J., 1924, **125**, 1564). Sonn, Hotes, and Sieg (*loc. cit.*) have also stated, without giving experimental details, that 1-methylglyoxaline condenses with formaldehyde mainly in the 2-position, and that 4 : 5-dibromo-1-methylglyoxaline does not condense with formaldehyde. It would thus appear from previous work that glyoxalines with a free imino-group give 4(5)-hydroxymethyl deriv-

atives, and *N*-methylated glyoxalines give 2-hydroxymethyl derivatives, whilst the accumulation of acidic groups in the molecule, as in 4 : 5-dibromo-1-methylglyoxaline, prevents condensation. The present investigation was carried out with the object of amplifying the experimental material, and the results are in harmony with the conclusions summarised above, except that it has been shown that an *N*-methylated glyoxaline may yield a 5-hydroxymethyl derivative. The ready condensation of 5-chloro-1-methylglyoxaline with formaldehyde reported by previous investigators (*supra*) was confirmed, and in our hands the yield of 5-chloro-1-methyl-2-hydroxymethylglyoxaline was 89%, but attempts to condense the isomeric 4-chloro-1-methylglyoxaline with formaldehyde under similar conditions were unsuccessful, 4-chloro-1-methylglyoxaline being recovered unchanged to the extent of 60%. As an example of an unmethylated 4(5)-halogen-substituted glyoxaline, 4(5)-bromoglyoxaline was available and this was found to give a poor yield of 4(5)-*bromo*-5(4)-*hydroxymethylglyoxaline* (I) together with some unchanged base and much amorphous material. The constitution of the product (I) was established through its reduction by hydriodic acid and phosphorus to 4(5)-methylglyoxaline (II).

(I.) (II.)

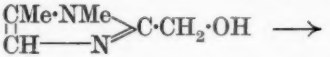
Next, the effect of the more strongly polar nitro-group was examined, and the condensation of 4(5)-nitroglyoxaline and its two isomeric *N*-methyl derivatives with formaldehyde was attempted; 4(5)-nitroglyoxaline and 4-nitro-1-methylglyoxaline were then recovered unchanged to the extent of more than 90%. 5-Nitro-1-methylglyoxaline was recovered unchanged to the extent of 68% only, this indicating that some condensation had taken place, although the presumed condensation product could not be isolated in a pure state. The condensation of the two *N*-methyl derivatives of 4(5)-methylglyoxaline was then studied. 1 : 4-Dimethylglyoxaline condensed with formaldehyde, giving a 44% yield of 1 : 4-*dimethyl*-5-*hydroxymethylglyoxaline* (III), the constitution of this product being proved through its reduction by hydriodic acid and phosphorus to the 1 : 4 : 5-trimethylglyoxaline (IV) previously made by Jowett (J., 1905, **87**, 405) by the methylation of 4 : 5-dimethylglyoxaline.



(III.) (IV.) (V.)

In earlier attempts to orient the base (III), 4(5)-methyl-5(4)-hydroxymethylglyoxaline was methylated, a mixture of (III)

with the isomeric 1 : 5-dimethyl-4-hydroxymethylglyoxaline (V) being expected. The only methylation product isolated in a pure state was not identical, but isomeric, with (III) and is consequently 1 : 5-*dimethyl*-4-*hydroxymethylglyoxaline* (V). The condensation of 1 : 5-dimethylglyoxaline with formaldehyde, however, did not give rise to this product but to an isomeride, which must consequently be 1 : 5-*dimethyl*-2-*hydroxymethylglyoxaline* (VI). Its constitution was confirmed by reduction, a trimethylglyoxaline being thus obtained which was not identical with 1 : 4 : 5-trimethylglyoxaline, and must consequently be 1 : 2 : 5-*trimethylglyoxaline* (VII).

(VI.)  (VII.)

The condensation of 1-methylglyoxaline with formaldehyde gave 1-*methyl*-2-*hydroxymethylglyoxaline* (VIII) as stated by Sonn, Hotes, and Sieg (*loc. cit.*), the yield being more than 60%. The constitution of this base was established through its reduction to 1 : 2-dimethylglyoxaline (IX).

(VIII.) (IX.)

Finally, the condensation of glyoxaline with formaldehyde was studied, but no crystalline products could be isolated.

Experimental.

Condensation of Glyoxalines with Formaldehyde.—The general method of procedure was as follows: The glyoxaline base and 40% aqueous formaldehyde (abbreviated below to formaldehyde) were enclosed in a sealed tube or pressure bottle and heated in an oil-bath. Except in the cases of 4(5)-nitroglyoxaline and 4-nitro-1-methylglyoxaline, the products were worked up by adding picric acid (1 mol.) in hot aqueous solution; as a rule, resinous picrates then separated first, followed by the crystalline picrates of the hydroxymethyl compound and of the unchanged glyoxaline in this order. The identity of the material recovered unchanged was established in each case by the mixed m. p. method.

4(5)-*Nitroglyoxaline and Formaldehyde.*—(*a*) 4(5)-Nitroglyoxaline (7·0 g.) and formaldehyde (10 c.c.; 2·3 mols.) were heated for 3 hours at 125°. The base was then mainly undissolved, and after washing with water and crystallisation from glacial acetic acid, 6·83 g. of unchanged 4(5)-nitroglyoxaline, m. p. 311—312° (corr.), were recovered; yield, 97·6%.

(*b*) 4(5)-Nitroglyoxaline (2·0 g.) and formaldehyde (2·8 c.c.; 2·2 mols.), heated for 6 hours at 150°, gave 1·92 g. of recovered 4(5)-nitroglyoxaline, m. p. 310—312° (corr.); yield, 96·0%.

4-*Nitro*-1-*methylglyoxaline and Formaldehyde.*—4-Nitro-1-methylglyoxaline (1·08 g.) and formaldehyde (1·9 c.c.; 3 mols.) were heated for 5 hours at 135°. The base was then mainly undissolved, and after crystallisation from water 0·98 g. of unchanged 4-nitro-1-methylglyoxaline, m. p. 134° (corr.), was recovered; yield, 90·8%.

5-*Nitro*-1-*methylglyoxaline and Formaldehyde.*—(*a*) 5-Nitro-1-methylglyoxaline (0·65 g.) and formaldehyde (1·6 c.c.; 4 mols.) were heated for 5 hours at 125°. The product gave with hot aqueous picric acid, first resinous picrates, then crude 5-nitro-1-methylglyoxaline picrate. This was recrystallised from water, 0·64 g., m. p. 151—152°, and 0·60 g., m. p. 149—151°, being obtained; yield, 68·1%.

(*b*) A similar result was obtained on heating the reactants for 6 hours at 130°, 5-nitro-1-methylglyoxaline picrate being recovered in 52% yield together with a resinous picrate. In both cases, the base and hydrochloride prepared from the resinous picrate failed to crystallise.

4(5)-*Bromoglyoxaline and Formaldehyde.*—This condensation was carried out under various conditions as shown below, and the products were worked up as picrates. The fourth column gives the yield (*a*) of 4(5)-bromo-5(4)-hydroxymethylglyoxaline isolated as pure picrate, and the fifth the yield (*b*) of 4(5)-bromoglyoxaline recovered as pure picrate. Considerable quantities of resinous picrates were also obtained.

Mols. CH_2O used.	Duration of heating (hrs.).	Temp.	*a*, %.	*b*, %.
2·5	2	110°	Nil	98·1
3	1	150	,,	53·7
1·5	2	150	,,	42·7
3	3	150	8·8	30·0
3	4	150	9·3	35·2
3	5	150	10·4	10·6
3	8	150	0·3	Nil
3	3½	160	1·5	3·8

4(5)-*Bromo*-5(4)-*hydroxymethylglyoxaline* (I) crystallises from alcohol in colourless plates, m. p. 116—117° (corr.), which contain $\frac{1}{2}H_2O$ (Found, in air-dried base: loss at 80°, 5·3. $C_4H_5ON_2Br,\frac{1}{2}H_2O$ requires H_2O, 4·8%. Found in dried base: C, 26·9; H, 3·0. $C_4H_5ON_2Br$ requires C, 27·1; H, 2·8%). It is sparingly soluble in cold water, readily soluble in alcohol, acetone, or chloroform, but insoluble in ether or benzene. The *hydrochloride* crystallises from alcohol in colourless prisms, m. p. 157° (corr.; eff.) [Found in salt dried at 100° (loss 0·8%): C, 22·5; H, 2·8. $C_4H_5ON_2Br,HCl$ requires C, 22·5; H, 2·8%]. It is very easily soluble in water, and easily soluble in hot alcohol or concentrated hydrochloric acid.

The *picrate* crystallises from water in yellow, lustrous, serrated

needles, containing $1H_2O$, which is lost at 95° but not in a vacuum over sulphuric acid at the ordinary temperature. The dried salt has m. p. 180° (corr.). It is sparingly soluble in cold water, but readily soluble in hot water, alcohol, or acetone (Found in air-dried salt: loss at 95°, 4·5. $C_4H_5ON_2Br,C_6H_3O_7N_3,H_2O$ requires H_2O, 4·3%. Found in dried salt: C, 29·3; H, 2·2. $C_4H_5ON_2Br,C_6H_3O_7N_3$ requires C, 29·6; H, 2·0%).

Reduction. 4(5)-Bromo-5(4)-hydroxymethylglyoxaline hydrochloride (0·45 g.), hydriodic acid (1·9 c.c.; *d* 1·7), and red phosphorus (0·13 g.) were heated in a sealed tube for 5½ hours at 160°. The product was diluted with water, filtered, and extracted with chloroform whilst acid to remove impurities. The aqueous solution was then concentrated, saturated with potassium carbonate, and extracted first with chloroform, then with ether. The extracts were converted into picrates, and gave 0·55 g. of 4(5)-methylglyoxaline picrate, m. p. 159—160° (corr.), alone or mixed with a known specimen; yield, 83·9%.

4-*Chloro*-1-*methylglyoxaline and Formaldehyde.*—4-Chloro-1-methylglyoxaline (1·77 g.) and formaldehyde (5·5 c.c.; 4·8 mols.) were heated for 4 hours at 130°, and the product was converted into picrates; 3·16 g. of 4-chloro-1-methylglyoxaline picrate, m. p. 166°, were obtained (yield, 60·2%) together with a resinous picrate. The base and hydrochloride from the latter failed to crystallise.

5-*Chloro*-1-*methylglyoxaline and Formaldehyde.*—5-Chloro-1-methylglyoxaline (1·08 g.) and formaldehyde (2·4 c.c.; 3·5 mols.), heated for 8 hours at 135—140°, gave 5-chloro-1-methyl-2-hydroxymethylglyoxaline, isolated as picrate, m. p. 151° (corr.), in 89% yield. Sarasin (*loc. cit.*) and Sonn, Hotes, and Sieg (*loc. cit.*) record yields of 95 and 80% respectively.

1 : 4-*Dimethylglyoxaline and Formaldehyde.*—1 : 4-Dimethylglyoxaline (10·6 g.) and formaldehyde (22·3 c.c.; 3 mols.) were heated for 6 hours at 125°, and the product was converted into picrates and crystallised fractionally from water and methyl alcohol; 17·5 g. of pure 1 : 4-dimethyl-5-hydroxymethylglyoxaline picrate (yield, 44·6%) were obtained together with 1·43 g. of pure 1 : 4-dimethylglyoxaline picrate (yield, 4·0%).

1 : 4-*Dimethyl-5-hydroxymethylglyoxaline* (III) crystallises from absolute alcohol in small, colourless prisms, m. p. 126—127° (corr.) (Found: C, 57·0; H, 8·0; N, 22·0. $C_6H_{10}ON_2$ requires C, 57·1; H, 7·9; N, 22·2%). It is very readily soluble in water or alcohol, readily soluble in chloroform, but very sparingly soluble in ether.

The *hydrochloride* crystallises from concentrated hydrochloric acid in colourless plates, m. p. 145° (corr.), which are very hygroscopic.

The *hydrogen oxalate* crystallises from absolute alcohol in colourless prisms, m. p. 106—107° (corr.) (Found: C, 44·6; H, 5·6. $C_6H_{10}ON_2,C_2H_2O_4$ requires C, 44·4; H, 5·6%). It is very readily soluble in water, less soluble in cold alcohol.

The *picrate* crystallises from water in yellow prisms, m. p. 167—168° (corr.), which suffer no loss at 110°. It is sparingly soluble in cold water, alcohol, or acetone, but readily soluble in the hot solvents. Attempts to estimate carbon and hydrogen in this salt were frustrated by explosions.

Reduction. 1 : 4-Dimethyl-5-hydroxymethylglyoxaline (0·63 g.), hydriodic acid (1·5 c.c.; *d* 1·7), and red phosphorus (0·082 g.) were heated in a sealed tube for 6 hours at 160°. The product was diluted with water, filtered, made strongly alkaline with sodium hydroxide, and extracted with chloroform and ether. The extracts were converted into picrates and gave 1 : 4 : 5-trimethylglyoxaline picrate in 79% yield (1·26 g., m. p. 218—219°, + 0·08 g., m. p. 215—216°). This salt was identified by the mixed m. p. method, with the help of a specimen of 1 : 4 : 5-trimethylglyoxaline picrate, m. p. 218°, prepared by Jowett (J., 1905, **87**, 405) for which we are indebted to the Wellcome Chemical Research Laboratories. The salt was also analysed (Found: C, 42·7; H, 3·9. Calc.: C, 42·9; H, 3·8%), and from it the base was prepared. This was not completely purified (it had m. p. 39—40°; Jowett gives 46°), but was converted into the chloroaurate. This had m. p. 201° (corr.) (Jowett gives 202°) (Found: Au, 43·6. Calc.: Au, 43·8%).

1 : 5-*Dimethylglyoxaline and Formaldehyde.*—1 : 5-Dimethylglyoxaline (1·4 g.) and formaldehyde (4·9 c.c.; 4·5 mols.) were heated for 6 hours at 130° and the product was converted into picrates, 1·75 g. of pure 1 : 5-dimethyl-2-hydroxymethylglyoxaline picrate (yield, 33·8%) and 2·06 g. of 1 : 5-dimethylglyoxaline picrate, m. p. 163—164° (yield, 43·5%), being isolated. Under milder conditions (4 hours at 115—120°) no condensation product was isolated, but 1 : 5-dimethylglyoxaline was recovered as picrate in 83% yield.

1 : 5-*Dimethyl*-2-*hydroxymethylglyoxaline* (VI) crystallises from absolute methyl alcohol in colourless, hexagonal plates, m. p. 126—127° (corr.) (Found in air-dried base: loss at 110°, 4·1. $C_6H_{10}ON_2,\frac{1}{2}H_2O$ requires H_2O, 6·7%. Found in dried base: C, 57·4; H, 7·9. $C_6H_{10}ON_2$ requires C, 57·1; H, 7·9%). It is very readily soluble in water, readily soluble in methyl or ethyl alcohol or chloroform, but very sparingly soluble in ether. A mixture of approximately equal parts of this base and 1 : 4-dimethyl-5-hydroxymethylglyoxaline, which also melts at 126—127°, had m. p. 76—80°.

The *picrate* crystallises from water in small, yellow, anhydrous prisms, m. p. 174° (corr.) (Found: C, 40·7; H, 3·9; N, 19·6. $C_6H_{10}ON_2,C_6H_3O_7N_3$ requires C, 40·6; H, 3·7; N, 19·7%). It is sparingly soluble in cold water or alcohol.

Reduction. 1 : 5-Dimethyl-2-hydroxymethylglyoxaline (0·39 g.), hydriodic acid (0·9 c.c.; *d* 1·7), and red phosphorus (0·051 g.) were heated in a sealed tube for 6 hours at 160°. After dilution, filtration, and extraction with chloroform to remove impurities, the liquor was saturated with potassium carbonate and extracted with chloroform, which took up a brown mobile oil (0·37 g.) having a faint pyridine-like odour. This was converted into picrate; 1 : 2 : 5-trimethylglyoxaline picrate (0·97 g.; m. p. 204°; yield 92·2%) was then obtained.

1 : 2 : 5-*Trimethylglyoxaline picrate* (VII) crystallises from water in long, pale yellow, lustrous, anhydrous needles, m. p. 208—209° (corr.) (Found: C, 42·6; H, 4·0; N, 20·7. $C_6H_{10}N_2,C_6H_3O_7N_3$ requires C, 42·5; H, 3·8; N, 20·6%). It is sparingly soluble in cold water or alcohol. A mixture of approximately equal parts of this salt with 1 : 4 : 5-trimethylglyoxaline picrate (m. p. 218°) had m. p. 194—195°. The base prepared from the pure picrate did not crystallise, and was converted into the *chloroaurate*, which crystallised from dilute hydrochloric acid in orange-yellow, anhydrous plates, m. p. 186—187° (corr.) (Found: Au, 43·6. $C_6H_{10}N_2,HAuCl_4$ requires Au, 43·8%).

Methylation of 4(5)-*Methyl*-5(4)-*hydroxymethylglyoxaline.*—Attempts to methylate this base by heating with either methyl iodide or methyl sulphate failed, for no crystalline substance other than a small proportion of the unchanged material could be isolated (as picrate) from the reaction product, but methylation with methyl sulphate and aqueous sodium hydroxide was more successful.

4(5)-Methyl-5(4)-hydroxymethylglyoxaline (2·35 g.) was methylated by the gradual addition with shaking of 10% aqueous sodium hydroxide (23·6 c.c.) and methyl sulphate (2·4 c.c.). After the mixture had been kept for 2 hours, chloroform extracted a yellowish-brown, crystalline mass (0·8 g.), which was converted into picrate and this crystallised from water, 0·5 g. of pure 1 : 5-dimethyl-4-hydroxymethylglyoxaline picrate being obtained: yield, 6·7%.

1 : 5-*Dimethyl*-4-*hydroxymethylglyoxaline* (V) crystallises from absolute methyl alcohol in colourless, hexagonal plates, m. p. 164—165° (corr.) (Found: C, 57·2; H, 8·0. $C_6H_{10}ON_2$ requires C, 57·1; H, 7·9%). It is very readily soluble in water, and readily soluble in methyl or ethyl alcohol, acetone, or chloroform. The *picrate* crystallises from water in small, pale yellow, anhydrous prisms, m. p. 178—179° (corr.) (Found: C, 40·7; H, 3·7; N, 19·5.

$C_6H_{10}ON_2,C_6H_3O_7N_3$ requires C, 40·6; H, 3·7; N, 19·7%). It is sparingly soluble in cold water or alcohol.

1-*Methylglyoxaline and Formaldehyde.*—(*a*) 1-Methylglyoxaline (2·8 g.) and formaldehyde (4·6 c.c.; 3·5 mols.) were heated for 5 hours at 140°. The product was converted into picrates, and these crystallised fractionally from water. First, a molecular compound of 1-methyl-2-hydroxymethylglyoxaline picrate and 1-methylglyoxaline picrate (5·48 g.; m. p. 144—145°) separated, then 1-methyl-2-hydroxymethylglyoxaline picrate (4·42 g.; m. p. 137°). The yield of 1-methyl-2-hydroxymethylglyoxaline is thus 62·6%, whilst 24·6% of 1-methylglyoxaline was recovered unchanged. (*b*) 1-Methylglyoxaline (3·1 g.) and formaldehyde (4·4 c.c.; 3·0 mols.), heated for 4 hours at 130°, gave 11·35 g. of the picrate, m. p. 144—145°, and some 1-methylglyoxaline picrate (0·11 g.; m. p. 158°). The yield of 1-methyl-2-hydroxymethylglyoxaline is here 46·1%, whilst 47·0% of 1-methylglyoxaline was recovered unchanged.

1-*Methyl-2-hydroxymethylglyoxaline* (VIII) crystallises from chloroform in colourless prisms, m. p. 116° (corr.) [Found in base dried at 80° (loss 1·3%): C, 53·4; H, 7·0. $C_5H_8ON_2$ requires C, 53·6; H, 7·1%]. It is readily soluble in water or alcohol, soluble in hot acetone or chloroform, but insoluble in ether or benzene. It is not volatile in steam. The picrate crystallises from water in small, yellow, lustrous prisms, m. p. 138° (corr.) [Sonn, Hotes, and Sieg (*loc. cit.*) give m. p. 136—137° (uncorr.)] (Found: loss at 100°, 3·3. $C_5H_8ON_2,C_6H_3O_7N_3,\frac{1}{2}H_2O$ requires H_2O, 2·6%. Found in dried salt: C, 38·8; H, 3·2. $C_5H_8ON_2,C_6H_3O_7N_3$ requires C, 38·7; H, 3·2%). It is very sparingly soluble in cold water.

Reduction. 1-Methyl-2-hydroxymethylglyoxaline (0·7 g.), hydriodic acid (1·4 c.c.; *d* 1·7), and red phosphorus (0·06 g.) were heated at 155—160° for 5 hours, and the product was worked up in the usual way; 1:2-dimethylglyoxaline picrate (0·6 g.; yield 29·5%; m. p. 178—179°, alone or mixed with an authentic specimen for which we are indebted to the Wellcome Chemical Research Laboratories) was then obtained together with 1-methyl-2-hydroxymethylglyoxaline picrate (0·49 g.; yield 23·0%; m. p. 136—137°).

The *molecular compound* of 1-methyl-2-hydroxymethylglyoxaline picrate and 1-methylglyoxaline picrate crystallises from water in pale yellow needles, m. p. 145—146° (corr.) [Found in air-dried salt: loss at 100°, 1·1. $C_4H_6N_2,C_5H_8ON_2,(C_6H_3O_7N_3)_2,\frac{1}{2}H_2O$ requires H_2O, 1·4%. Found in dried salt: C, 38·8; H, 3·2; N, 21·7. $C_4H_6N_2,C_5H_8ON_2,(C_6H_3O_7N_3)_2$ requires C, 38·7; H, 3·1; N, 21·5%]. It is almost insoluble in cold water, but readily soluble in hot water. A mixture of this picrate with 1-methyl-2-hydroxy-

methylglyoxaline picrate (m. p. 138°) melted at 129—130°, whilst a mixture with 1-methylglyoxaline picrate (m. p. 159°) melted at 139—140°. On converting the picrate, m. p. 145—146°, into the corresponding bases and distilling with steam, 1-methylglyoxaline was carried over and 1-methyl-2-hydroxymethylglyoxaline remained unvolatilised. The separated bases were then converted into picrates and identified in the usual way. The constitution of the picrate, m. p. 145—146°, as an equimolecular compound of the picrates of 1-methyl-2-hydroxymethylglyoxaline and 1-methylglyoxaline was confirmed by preparing it from the two salts.

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CCCCXII.—*The Oxide-ring Structure of Normal and γ-Derivatives of Mannose. Preparation and Oxidation of Derivatives of γ-Mannonolactone and δ-Mannonolactone, with an Addendum on the Formulation of Normal and γ-Sugars as Derivatives of Pyran and Furan and the Suggestion of a New Nomenclature.*

By EDWARD HAGUE GOODYEAR and WALTER NORMAN HAWORTH.

IN continuing the study of lactones derived from sugars we have prepared several new derivatives in the mannose series. The ordinary γ-mannonolactone (III) was first prepared from mannonic acid by Fischer and Hirschberger (*Ber.*, 1889, **22**, 3218) and was obtained in purer condition by Nef (*Annalen*, 1914, **403**, 306) and by Hedenburg (*J. Amer. Chem. Soc.*, 1915, **37**, 345). The latter two authors also isolated an isomeric lactone, described originally as the "β" lactone, which is also obtainable from mannonic acid by adopting a different procedure for the anhydridation. We recommend that this "β" lactone should now be regarded as the δ-mannonolactone (VI) in view of the results obtained in a comparative study of lactones (compare Haworth and Nicholson, J., 1926, 1899). In the case of the parallel example from gluconic acid, the supposed "β" gluconolactone also should be described as δ-gluconolactone.

By solution of γ-mannonolactone in dry acetone containing 0·1% of hydrogen chloride, we have prepared the crystalline *γ-mannonolactone-monoacetone*, and under slightly different conditions the crystalline γ-mannonolactone-diacetone (II) has also been obtained. The latter is identical with the substance originally prepared by

Ohle and Berend (*Ber.*, 1925, **58**, 2590) from mannose-diacetone (I) by oxidation to the diacetone of mannonic acid, which, by loss of water, passes into the corresponding lactone. Specimens have been prepared by each of these methods and their identity established. The constitution (I) assigned to mannose-diacetone therefore receives confirmation.

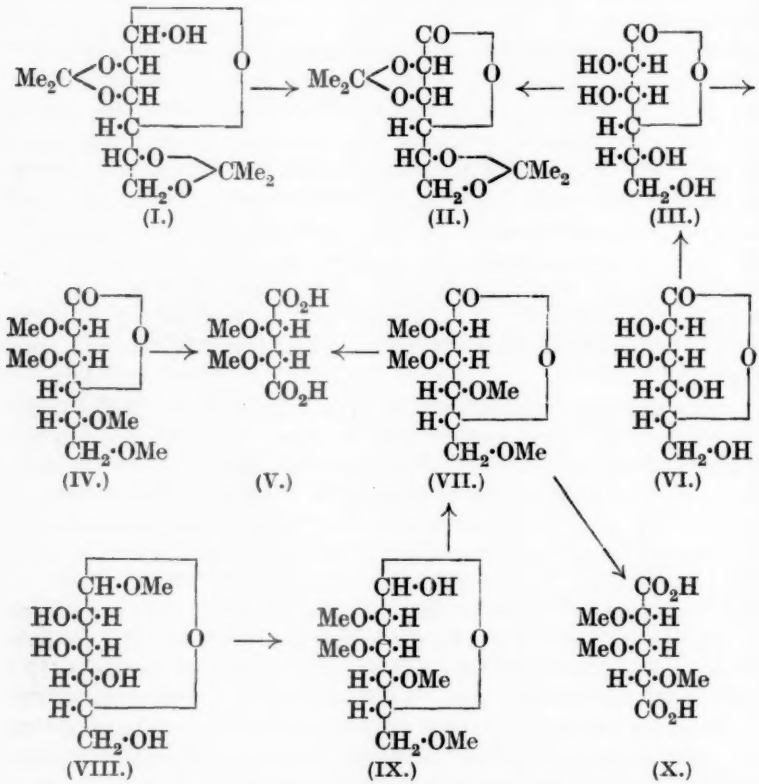
By methylation of γ-mannonolactone-monoacetone the crystalline *dimethyl γ-mannonolactone-monoacetone* was isolated, and on hydrolysis with dilute mineral acid this gave *dimethyl mannonolactone*. Acetylation of γ-mannonolactone gave rise to the *tetra-acetyl* derivative.

When γ-mannonolactone was methylated with methyl iodide and silver oxide in the presence of acetone, that is, under the conditions described by Levene and Simms (*J. Biol. Chem.*, 1925, **65**, 46), a mixture of crystalline products was obtained, from which were isolated (*a*) tetramethyl γ-mannonolactone (IV), which gave a crystalline *phenylhydrazide*, and (*b*) dimethyl γ-mannonolactone-monoacetone, identical with the specimen above-mentioned. When, however, acetone was avoided as a solvent during the methylation of γ-mannonolactone, only tetramethyl γ-mannonolactone was obtained. This showed $[\alpha]_D^{18°}$ + 65·2° falling to 61·2° in 9 days (compare Drew, Goodyear, and Haworth, this vol., pp. 1242—3).

In an attempt to prepare the tetramethyl derivative from δ-mannonolactone by direct methylation, we were only able to recognise in the products the tetramethyl γ-mannonolactone, and it seems clear that the 1 : 5 ring in the unsubstituted δ-lactone undergoes conversion into a 1 : 4 ring under the conditions employed. During the process of methylation, water is formed; this appears to open the lactone ring, which again closes to give the stable γ-lactone. The tetramethyl δ-mannonolactone was prepared, however, from α-methylmannoside (VIII) by the indirect method, namely, methylation followed by hydrolysis to normal tetramethyl mannose (IX) and oxidation of this sugar by means of bromine water. The tetramethyl δ-mannonolactone (VII) is isolated by conversion first into the crystalline phenylhydrazide, and after regeneration from this derivative is recognisable as a crystalline product, m. p. 23—25°, having $[\alpha]_D^{18°}$ + 150° (initial).

The constitution of each of these tetramethyl derivatives was determined by direct oxidation with nitric acid. Tetramethyl γ-mannonolactone (IV) gave on oxidation *i*-dimethoxysuccinic acid (V), which was identified as the crystalline methyl ester and as the crystalline *methylamide*, the latter being compared with a specimen prepared from *meso*tartaric acid by Haworth and Jones (this vol.,

p. 2352). This lactone should therefore be indexed as 2 : 3 : 5 : 6-tetramethyl mannonolactone (IV). The corresponding δ-lactone (VII) gave on oxidation a small yield of *i*-dimethoxysuccinic acid (V) and also, in a larger yield, *d*-arabo-trimethoxyglutaric acid (X), which was identified as the crystalline methylamide (m. p. 209)°. This was enantiomorphous with a specimen of the methylamide of the *l*-variety of the acid obtained by Haworth and Jones (*loc. cit.*), with which it was compared. This δ-lactone should therefore be indexed as 2 : 3 : 4 : 6-tetramethyl mannonolactone (VII).



The bearing of these results on the structure of the constituent sugars is evident. Since a lactone of formula (VII) is derived from tetramethyl mannose (IX), which in turn has been prepared from α-methylmannoside, it follows that the latter has a 1 : 5 or amylene oxide ring structure (VIII). Similarly it has been shown that mannose-diacetone is a derivative of γ-mannose (I) (Irvine and Skinner, J., 1926, 1089; compare Ohle and Berend, *loc. cit.*). This

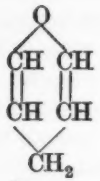
gives rise on oxidation to the same γ-mannonolactone-diacetone (II) as we have obtained direct from γ-mannonolactone (III), and since the latter gives on methylation a tetramethyl γ-mannonolactone of constitution (IV), it is demonstrated that the γ-mannose derivative has a constitution containing a butylene or 1 : 4 oxide ring. This conclusion is, however, dependent upon there having been no displacement of the ring during methylation of the γ-lactone, and this is unlikely to have occurred; and secondly upon there having been no such displacement during the introduction of acetone residues into the γ-mannonolactone. The latter contingency also is on the whole unlikely, because the γ-lactone contains two pairs of hydroxyl groups which are already favourably situated for *cis*-condensation with acetone residues and are also attached to contiguous carbon atoms. Moreover the γ-lactone is the stabilised form into which the δ-lactone is convertible.

The results now communicated assign to the mannose derivatives of the normal and the γ-series the same structural relationships as those of the normal and the γ-derivatives of glucose, of fructose, of arabinose, and of xylose, all of which have been shown by direct oxidation methods applied to their related lactones to be amylene oxides in their normal forms and butylene oxides in their labile or γ-forms (Avery, Haworth, and Hirst, this vol., p. 2308; Haworth, Hirst, and Learner, *ibid.*, p. 2432; Haworth, Hirst, and Miller, *ibid.*, p. 2436; Haworth and Jones, *loc. cit.*). In a later paper it will be shown that these same structural relationships have been fully proved also for galactose in its normal and γ-forms. So far, therefore, as it is possible to generalise from these direct oxidation results it is seen that the conclusions reached confirm entirely the structural formulæ which were adduced from a study of the comparative rates of hydrolysis of the two series of lactones in aqueous solution, as determined (*a*) by the polarimetric method (Drew, Goodyear, and Haworth, *loc. cit.*) and (*b*) by the conductivity method. The generalisation advanced by Charlton, Haworth, and Peat (J., 1926, 89), which stated that the normal sugars tend to exist in amylene oxide forms and the labile or γ-sugars in butylene oxide forms, is again supported by the collateral data obtained from the oxidation of the methylated lactones.

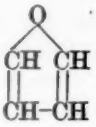
Addendum.

The normal sugars are thus seen to be representatives of the parent form indicated by pyran, and the labile or γ-sugars have as their parent substance furan. The two types of normal and labile sugars might well be described as the pyran- and furan-types. Thus, arabinose in its normal form is tetrahydroxytetrahydropyran

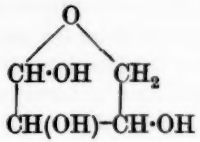
(A), whilst in its labile or γ-form it is tetrahydroxymethyltetrahydrofuran (B).



Pyran.

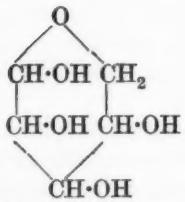


Furan.

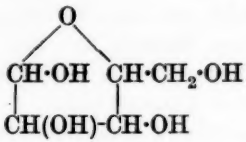


Furanose (a tetrose)
(Trihydroxytetrahydrofuran).

(A)



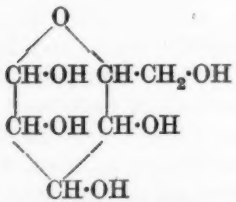
A Normal Pentose.
[Pyranose (Arabo-, etc.)].



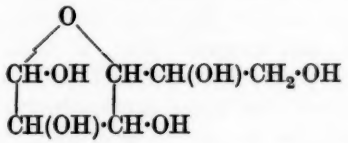
(B)

A γ-Pentose.
[Xylo-furanose (and also Arabo-, ribo-, lyxo-furanose)].

(C)



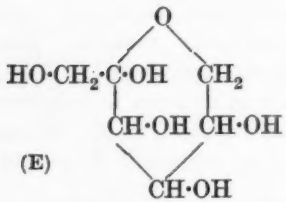
A Normal Aldo-hexose
[Gluco (etc.) -pyranose].



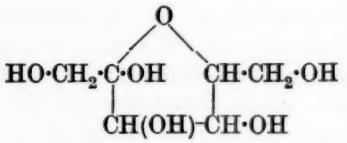
(D)

A γ-Aldo-hexose.
[Gluco (etc.) -furanose].

(E)



A Normal Keto-hexose.
[Fructo-pyranose].



(F)

A γ-Keto-hexose.
[Fructo-furanose].

There is urgent need for the adoption of a simplified, concise, standard nomenclature in the sugar group which will define the essential structural differences between a normal sugar form and a labile or so-called γ-sugar form. Such a revised nomenclature should be capable of expressing also the stereochemical relationships

of the various pentoses, hexoses, etc., which may occur in either structural form.

On the basis of the conclusions now reached, the formula (A) must be accepted as a general representation of a normal sugar, which might be described as a pyranose. The normal sugars arabinose, xylose, etc., may then be described as arabo-*pyrano*se, xylo-*pyrano*se, and both the structure and the configuration would be at once intelligible from this nomenclature. The corresponding labile or γ-isomerides may be described as arabo-*furano*se, xylo-*furano*se, etc. (B). Proceeding in a similar manner to the representation of a hexose, it is only necessary to modify the formula (A) by the introduction of a primary alcohol group as a side chain, in order to indicate (as a hexa-pyranose) the structural relationships of the normal hexoses, and this modification, having regard to both the structural and the stereochemical arrangement involved, would be recognisable under the name of gluco-*pyrano*se (C), manno-*pyrano*se, galacto-*pyrano*se, etc., whilst the labile or γ-sugars would similarly be described as gluco-*furano*se, manno-*furano*se, etc. (D).

Similarly in the cases of normal and γ-fructoses, which have been shown by one of us to have the constitutional formulæ (E) and (F), the corresponding nomenclature would apply: fructo-*pyrano*se for the normal sugar, and fructo-*furano*se for the labile form (Haworth and Hirst, J., 1926, 1858; Haworth, Hirst, and Learner, this vol., p. 1040; Haworth, Hirst, and Nicholson, *ibid.*, p. 1513; Avery, Haworth, and Hirst, *loc. cit.*; Haworth, Hirst, and Learner, this vol., p. 2432).

The sugars higher in the series, such as the heptoses, occurring in either form would be definable as hepta-*pyrano*ses or hepta-*furano*ses, the device which is already current being used for distinguishing between the configurations, namely, glucohepta-*pyrano*se, etc., instead of "glucoheptose (normal) of the amylene oxide form."

It is not without significance that the naturally occurring pigments such as the anthocyanins, occurring as glucosides, contain as an essential part of their structure a pyran residue, and that the anthoxanthins or hydroxyflavones contain the related pyrone group. It is conceivable that this residue is traceable to its origin as a normal sugar, suggesting that these colouring matters of plants are transformation products intimately related in their structure to the sugar group. The suggestion has already been made that phenols originate through an aldol type of condensation between the aldehyde group of an aldohexose of position (6) in the chain, giving a hexahydroxyhexahydrobenzene of the type of inositol, which then passes by elimination of water to the polyhydric phenols (Haworth, *J. Soc. Chem. Ind.*, 1927, **46**, 295). On the other

hand, the frequent occurrence of furan residues in natural products suggests that these are similarly traceable to the pre-existing γ-sugar. We have already shown that tetramethyl γ-fructose passes with remarkable ease into a furan derivative (Haworth, Hirst, and Nicholson, this vol., p. 1513).

Experimental.

Methylation of γ-Mannonolactone.—Crystalline γ-mannonolactone, prepared by the methods described by Nef and by Hedenburg (*loc. cit.*), was methylated with methyl iodide and silver oxide in presence of methyl alcohol as solvent. The product was treated with the same reagents in the presence of acetone (Levene and Simms, *J. Biol. Chem.*, 1925, **65**, 46) and thereafter twice with the methylating agents without any extraneous solvent; it then became partly crystalline. This product was distilled under diminished pressure, subjected to two further methylations, and again distilled. The major portion (70% yield), b. p. 100—105°/0·06 mm., became partly crystalline and the crystals were collected on porous tile and recrystallised from light petroleum (voluminous needles, m. p. 109—110°). A second crop consisted of both needles and plates, m. p. 83°. Recrystallisation of the latter from boiling carbon tetrachloride gave prisms, m. p. 110°, showing no depression of melting point in admixture with the needles. This material gave OMe, 30·25%. It was clear that the compound crystallising in needles could also be obtained from carbon tetrachloride in the form of prisms. It showed $[\alpha]_D^{20°}$ + 64·2° in water (c = 1·1), changing to + 55·8° in 9 days (Found: C, 53·5; H, 7·3. $C_{11}H_{18}O_6$ requires C, 53·6; H, 7·3%). These analytical figures agree with those required for a *monoacetone* derivative of dimethyl γ-mannonolactone, and that this was actually the product obtained was shown by an alternative method of preparation which is described later.

In order to investigate the reason for the occurrence of this compound a further lot of γ-mannonolactone was methylated (*a*) in the presence of acetone, and a further quantity (*b*) in the absence of acetone, only methyl alcohol being used as the extraneous solvent. In the former case, the same mixture of products was isolated, the chief of these being the compound, m. p. 110°, but in the latter case (*b*) an apparently homogeneous product was obtained, m. p. 108°, from ligroin; $[\alpha]_D^{18°}$ + 65·2° in water (c = 1·038), falling to 61·2° after 9 days; $[\alpha]_{5461}^{18°}$ + 77·0°, falling to 71·8° in 9 days (Found: C, 51·1; H, 7·6; OMe, 52·2. Calc. for $C_{10}H_{18}O_6$: C, 51·25; H, 7·7; OMe, 54·2%). This substance was obtained either as colourless plates or as long, transparent needles 1—2 cm. in length. Both forms had the same melting point.

When heated with phenylhydrazine, this product, which appeared to be the genuine tetramethyl γ-mannonolactone, gave a crystalline *phenylhydrazide*, m. p. 167° (from ether) (Found: C, 55·5; H, 7·6; OMe, 32·9; N, 8·4. $C_{16}H_{26}O_6$ requires C, 56·1; H, 7·6; OMe, 36·3; N, 8·2%). These analytical data suffice to show that the substance was the phenylhydrazide of a tetramethylmannonic acid.

γ-Mannonolactone-monoacetone.—γ-Mannonolactone was shaken with dry acetone containing a trace of hydrogen chloride (about 0·1%). Complete solution occurred in 20 minutes, and then the mineral acid was neutralised with silver carbonate. After filtration and evaporation, colourless crystals, m. p. 132°, were collected and also a second crop, m. p. 117° (impure diacetone derivative). Recrystallisation of the former product from acetone and ligroin gave colourless needles (yield, 85%), m. p. 133°; $[\alpha]_D^{20°}$ + 55·4° in water (c = 1·62) (Found: C, 49·1; H, 6·6. $C_9H_{14}O_6$ requires C, 49·5; H, 6·4%).

γ-Mannonolactone-diacetone.—Finely divided γ-mannonolactone (6 g.) was shaken with 400 c.c. of dry acetone containing 0·2% of hydrogen chloride. After 3 hours, when most of the lactone had dissolved, the mineral acid was removed with silver carbonate and the acetone evaporated under diminished pressure. Extraction of the crystalline residue with large volumes of light petroleum yielded colourless crystals, m. p. 122—125°; after recrystallisation from ligroin, m. p. 126°. $[\alpha]_D^{20°}$ + 50·6° in chloroform (c = 1); + 73·65° in 50% alcohol, falling to 45·9° after 20 days (Found: C, 55·8; H, 7·15. Calc. for $C_{12}H_{18}O_6$: C, 55·8; H, 7·0%). The melting point and physical constants agreed with those of γ-mannonolactone-diacetone observed by Ohle and Berend (*Ber.*, 1925, **58**, 2590) and the substance was identical with a specimen prepared by their method.

Dimethyl γ-Mannonolactone-monoacetone.—The above specimen of γ-mannonolactone-monoacetone was methylated by means of silver oxide and methyl iodide. The product crystallised from ether in bulky needles, m. p. 110°, and this was found to be identical with the product obtained above during the methylation of γ-mannonolactone in the presence of acetone (Found: OMe, 25·5. Calc.: OMe, 25·3%).

Dimethyl γ-Mannonolactone.—Hydrolysis of the above product with 0·1% aqueous hydrochloric acid gave a crystalline substance which crystallised from ethyl acetate–light petroleum in white needles, m. p. 109—110°; $[\alpha]_D^{20°}$ + 61·1° in water (c = 1·03), falling to 60·5° in 19 days. Yield, 60%. This was *dimethyl γ-mannonolactone* (Found: C, 46·6; H, 7·1; OMe, 28·9. $C_6H_{14}O_6$ requires C, 46·6; H, 6·8; OMe, 30·1%).

Tetra-acetyl γ-Mannonolactone.—A mixture of γ-mannonolactone

(1·g.), acetic anhydride (5 g.), and dry pyridine (6·7 g.) was shaken for 45 minutes until a clear solution was obtained, and this was kept in a stoppered vessel in the ice-chest for 2 days. After dilution with 50 c.c. of cold chloroform the solution was poured on powdered ice. The chloroform extract of this product was washed with water and sodium carbonate solution, dried, and evaporated. This gave a syrup which crystallised from ether in needles, m. p. 115—117°; the yield was 0·5 g. Recrystallisation from dry ether raised the m. p. to 120°. $[\alpha]_D$ + 44·9° in chloroform (c = 1·56) (Found: C, 48·6; H, 5·3. $C_{14}H_{18}O_{10}$ requires C, 48·55; H, 5·2%). This appeared to be the tetra-acetyl derivative of γ-mannonolactone.

Attempted Preparation of Derivatives of δ-Mannonolactone.—This crystalline substance, first described by Nef (*loc. cit.*) as β-mannonolactone, was prepared by Nef's method as modified by Hedenburg (*loc. cit.*). M. p. 162° (after recrystallisation from boiling ethyl alcohol); $[\alpha]_D^{20°}$ + 114·0° in water (c = 1·24), falling to + 27·5° after 21 hours. 20 G. of pure calcium mannonate gave 6·5 g. of this lactone.

This substance was treated with methyl iodide and silver oxide twice in the presence of methyl alcohol and once in the presence of acetone. The semi-crystalline product was drained on a tile and extracted with light petroleum, which removed a mobile liquid having $n_D^{18°}$ 1·4370. The crystals (m. p. 108°) showed no depression of m. p. in admixture with the specimen of tetramethyl γ-mannonolactone (Found: OMe, 52·2. Calc.: OMe, 54·2%). It thus appeared that the δ-lactone had been transformed into a γ-lactone during condensation with acetone which had been used as solvent in the methylation process.

Oxidation of Tetramethyl γ-Mannonolactone.—This crystalline lactone (1·5 g.) was heated with 13 c.c. of nitric acid (d 1·42) at 100° for about 15 minutes in order to initiate the oxidation. The bath was maintained at 95—100° for a further 7 hours, and the solution was then cooled and diluted, and the nitric acid removed as completely as possible by distillation under diminished pressure, followed by repeated dilution and further distillation. The syrupy residue, which contained crystals, was esterified with 4% methyl-alcoholic hydrogen chloride, and the product (0·85 g.) distilled under 0·1 mm.: Fraction I, from bath at 110—115°; 0·25 g., which crystallised immediately. Fraction II, bath at 115—120°; 0·4 g., which crystallised on nucleation with methyl dimethoxysuccinate. Fraction III, bath at 120—140°; 0·1 g., which was partly crystalline.

Fractions I and II were identical, since each gave on recrystallisation from light petroleum a crystalline ester, m. p. 68°, which was

identical with a specimen of methyl ester prepared from *meso*-tartaric acid, and this was confirmed by a mixed m. p. determination. The substance was therefore methyl *i*-dimethoxysuccinate (Found: C, 46·45; H, 9·6; OMe, 59·3. Calc.: C, 46·6; H, 9·6; OMe, 60·1%).

0·1 G. of this compound was converted into the methylamide by dissolving it in a saturated solution of methylamine in methyl alcohol. Crystals separated after 2 days, m. p. after recrystallisation 209°, giving no depression in admixture with *i*-dimethoxysuccinomethylamide prepared from *meso*tartaric acid by Haworth and Jones (*loc. cit.*) (Found: C, 47·1; H, 7·6; N, 13·1. Calc.: C, 47·1; H, 7·8; N, 13·7%).

Oxidation of Tetramethyl δ-Mannonolactone.—Crystalline 2 : 3 : 4 : 6-tetramethyl δ-mannonolactone (2·7 g.) prepared by the method described by Drew, Goodyear, and Haworth (this vol., p. 1243) was oxidised by digestion at 90° with 20 c.c. of nitric acid (*d* 1·42). The reaction proceeded smoothly, and after 4½ hours the evolution of brown fumes had ceased and a colourless solution remained. After dilution the nitric acid was repeatedly evaporated at 40° in a vacuum with addition of water, and finally a syrup was obtained which was dissolved in 80 c.c. of methyl-alcoholic hydrogen chloride (3·5%) and digested at 70° for 6 hours. The cooled solution was neutralised with silver carbonate, and the ester obtained (2·3 g.) by the usual method of isolation. This distilled at 95—100°/0·07 mm. and showed $[\alpha]_D^{18^\circ}$ − 27·3° (in water, c = 1·21). The ester gave on solution in methyl-alcoholic ammonia the crystalline amide, m. p. 255°. The ester was, however, identified by means of the following preparation of the crystalline methylamide.

The liquid ester (0·5 g.) was dissolved in methyl alcohol, and the solution was saturated with methylamine. Having been kept for 2 days, the solution was evaporated and gave a solid residue which was recrystallised from ethyl acetate. The first crop of crystals (0·14 g.) had m. p. 155—160° and obviously contained a slight impurity, which was removed on a further crystallisation from the same solvent. This gave a colourless, crystalline product (0·04 g.), m. p. 208—209°, identical with the specimen of *i*-dimethoxysuccinomethylamide prepared by Haworth and Jones from *meso*-tartaric acid. A second crop of crystals was obtained by concentrating all the mother-liquors; colourless needles (0·3 g.), m. p. 172°. This substance was recognised as *d*-arabo-trimethoxyglutaromethylamide, $[\alpha]_D^{18^\circ}$ − 59·7° in water (c = 0·94), the enantiomorph of the *l*-variety described by Haworth and Jones (*loc. cit.*) as having m. p. 172°, $[\alpha]_D^{18^\circ}$ + 59·9° in water (c = 1) (Found: C, 48·3; H, 8·3; N, 11·0; OMe, 36·3. Calc.: C, 48·35; H, 8·1; N, 11·2; OMe, 37·5%).

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EDGBASTON.

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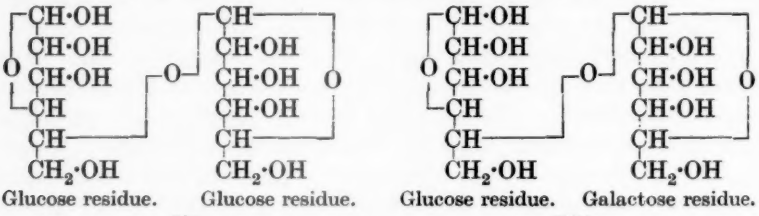
CCCCXIII.—*The Constitution of the Disaccharides. Part XVII. Maltose and Melibiose.*

By WALTER NORMAN HAWORTH, JOHN VAUGHAN LOACH, and CHARLES WILLIAM LONG.

THE problem of the structure of maltose and melibiose has excited unusual controversy and various rival formulæ appear in the literature from time to time intended to supplant those submitted by one of us. The most recent of these attempts to reconstruct the constitution of these disaccharides is that made by Irvine in the published transcript of an address to the American Chemical Society (*Chemical Reviews*, 1927, **4**, 203). Without contributing any fresh evidence, Irvine has now advocated the following scheme, wherein maltose is given formula (I) and melibiose is given formula (II) :

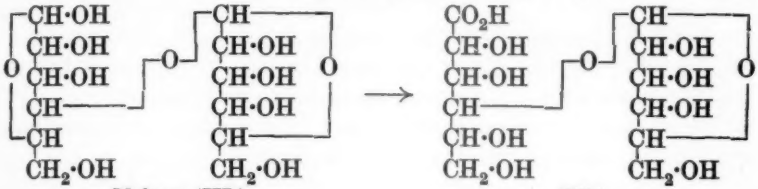


(I.) (II.)

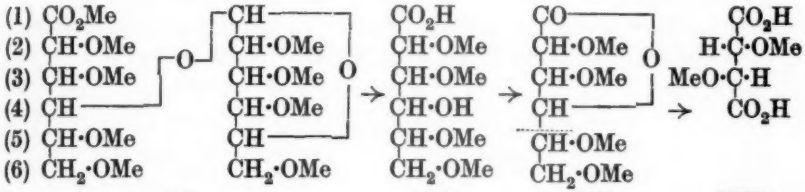
It is to be noticed that the revised structural form initially advocated by one of us for glucose in its normal derivatives is adopted for the non-reducing residue in (I), whilst the reducing glucose component in each disaccharide is given the character of a butylene oxide form which one of us applied to γ-glucose derivatives. Thus the effect of these new attempts to represent these disaccharides is to emphasise that each of them contains as its reducing hexose component a labile or γ-glucose residue. No evidence is given for the hypothesis that either maltose or melibiose is a γ-sugar, nor indeed do the properties of these disaccharides warrant that such an assumption need be entertained.

These views advanced by Irvine are indeed capable of simple and complete investigation, and in the case of maltose they have already been shown to be invalid by Haworth and Peat (J., 1926,

3094). The latter authors have demonstrated that maltose has the constitution (III), since it gives on oxidation a maltobionic acid which can only be formulated as in (IV). Completely methylated maltobionic ester (V) yields on hydrolysis only tetramethyl glucose and the tetramethyl gluconic acid (VI) which forms the γ-lactone (VII), and the structure of the latter has been proved by its oxidation to *d*-dimethoxysuccinic acid (VIII) and not to xylo-trimethoxyglutaric acid (Haworth, Hirst, and Miller, this vol., p. 2436), which is obtained from the corresponding tetramethyl δ-gluconolactone.



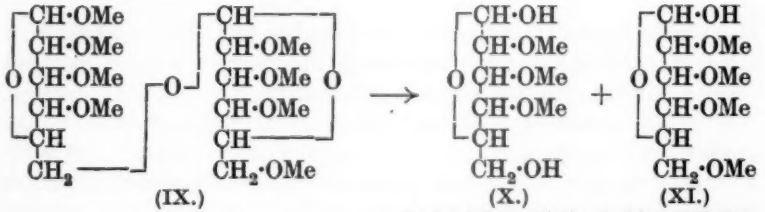
Maltose (III.) (IV.)



(V.) (VI.) (VII.) (VIII.)

These facts leave no room for doubt that the biose linking in maltose is situated at position 4 in the reducing biose. If this result is compared with that furnished by the isolation of 2 : 3 : 6-trimethyl glucose as a cleavage product of fully methylated maltose (Irvine and Black, J., 1926, 862; Cooper, Haworth, and Peat, *ibid.*, p. 876), the oxide ring of this hexose unit is seen to be present at the 5th carbon atom as shown in the maltose structure (III).

The case of melibiose is capable of a similar demonstration. Methylated melibiose (IX) yields on hydrolysis two cleavage products, one of which (XI) is crystalline, and the other, a liquid (X), yields a crystalline glucoside.



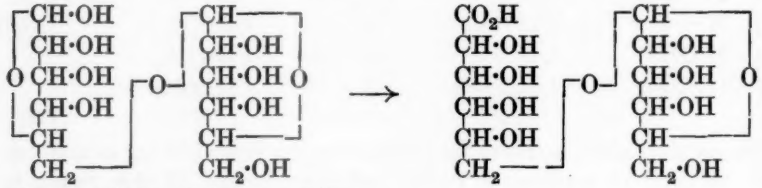
(IX.) (X.) (XI.)

2 : 3 : 4-Trimethyl glucose. 2 : 3 : 4 : 6-Tetramethyl galactose.

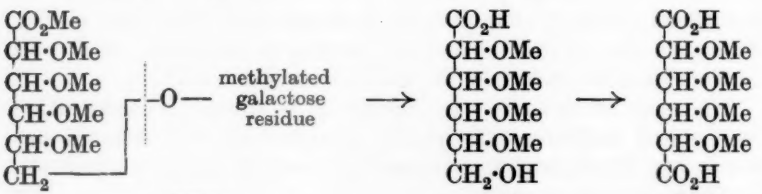
The inference was therefore drawn by Charlton, Haworth, and Hickinbottom (this vol., p. 1527) that the constitution (XII) should be allocated to melibiose, and the same formula was also supported by the earlier work of Haworth, Hirst, and Ruell on raffinose (J., 1923, **123**, 3125), and still earlier by Haworth and Leitch (J., 1918, **113**, 188).

This formula for melibiose is finally established by an alternative proof wherein melibionic acid (XIII) has been methylated to give methyl octamethylmelibionate (XIV), which on hydrolysis yields, besides crystalline 2 : 3 : 4 : 6-tetramethyl galactose, the 2 : 3 : 4 : 5-tetramethyl gluconic acid (XV) which does not form a lactone. The structure of the latter product has been determined by its oxidation with nitric acid to tetramethylsaccharic acid (XVI), which gives a crystalline methyl ester identical in every respect with that obtained by methylating saccharic acid.

It is therefore demonstrated that since 2 : 3 : 4 : 5-tetramethyl gluconic acid (XV) is the only product isolated which corresponds to the glucose component of melibiose, this component is attached to the galactose residue through the hydroxyl in position 6.



Melibiose (XII.) (XIII.)



(XIV.) (XV.) (XVI.)

The structural formula assigned by one of us to melibiose (XII) thus receives substantial confirmation from these new experimental results, as does also our formula for raffinose.

Another aspect of the constitution of this disaccharide is the stereochemical signification given to it in the current literature as a glucose-β-galactoside, a conclusion based on the observation that melibiose is said to undergo slow hydrolysis with emulsin (Fischer and Armstrong, *Ber.*, 1902, **35**, 3144). Helferich and

Rauch, however, have synthesised a biose of this configuration and structure, and the specific rotations both of the sugar and of its octa-acetate indicate its non-identity with melibiose (*Ber.*, 1926, **59**, 2655). Other considerations serve to show also that the stereochemical characterisation of this sugar revealing the presence of a β-biose junction between the two hexose residues is unsound. This has been argued in a previous paper (Charlton, Haworth, and Hickinbottom, *loc. cit.*) wherein it is suggested that melibiose may be a glucose-α-galactoside corresponding to maltose, which is a glucose-α-glucoside.

The argument may be supplemented by the new data now made available in the present experimental work. The methylated esters of the monobasic acids corresponding to each of the disaccharides, maltose, cellobiose, lactose, melibiose, have been prepared and their specific rotations are given, and in addition the rotation changes consequent upon their hydrolysis to the constituent hexoses and hexonic acids have been recorded. Each of these methylated esters may be regarded, for the purpose of comparison, as the equivalent of a methylglucoside or a methylgalactoside which may be recognised either as an α- or a β-form. In the case of the simple methylhexosides the magnitude of rotation alone is accepted as a sufficient indication of stereochemical homogeneity. If the analogous principle be conceded also for the methylated esters of the various bionic acids, the data now collected may be valuable evidence of the stereochemical nature of the bionic junction between the gluconic acid residue and the remaining hexose in a bionic acid, and, by inference, of the character also of the biose junction in the parent disaccharide. It may be mentioned that methylation of α-methylglucoside, etc., does not appear materially to effect interchange into the β-methylglucoside.

	$[\alpha]_D$.		Equilibrium attained on hydrolytic cleavage.
(1) Methyl octamethylmaltobionate ...	+121°	→	+54·9°
(2) Methyl octamethylcellobionate ...	+ 5	→	+55
(3) Methyl octamethyl-lactobionate ...	+ 34	→	+77·2
(4) Methyl octamethylmelibionate ...	+106	→	+64

The significance of these figures is the comparatively small magnitude of rotation of the substances Nos. 2 and 3, which are the products from the authenticated β-bioses, namely, cellobiose, which is glucose-β-glucoside, and lactose, which is glucose-β-galactoside. It may be further observed that these low rotation values show an increase when the ester is hydrolysed to the constituent hexose and hexonic acid. The equilibrium rotation value of the hexose is known already from previous experiments, whilst the specific

rotations of the methylated hexonic acids are also known (Drew, Goodyear, and Haworth, this vol., p. 1237).

	$[\alpha]_D$.	
Tetramethyl glucose	84°	(at equil.)
„ galactose	+117	(at equil.)
2 : 3 : 5 : 6-Tetramethyl gluconic acid	+ 27	
2 : 3 : 4 : 5- „ „ „	+ 10	

Inspection of the figures available for cases Nos. 1 and 4 reveals a striking similarity between these two derivatives of maltose and melibiose, inasmuch as both the esters have initially a high specific rotation which declines to a lower value on hydrolysis. The inference which might be drawn is therefore that in each of these examples the α-linking of a glucoside is undergoing cleavage to the hexonic acid and to the α + β-equilibrated mixture of the methylated hexose.

If this evidence be considered to provide a valid argument for the case of melibiose, it will then be clear that this disaccharide is not a glucose-β-galactoside, which is the view commonly accepted on the basis of Fischer and Armstrong's observation, but is a glucose-α-galactoside.

Discussion of Results.

With the present work there is now concluded a survey of the constitution of the six commonly occurring disaccharides—sucrose, cellobiose, maltose, gentiobiose, lactose, and melibiose—and the structural classification of these may now be reviewed in the light of these new data, and of the controversy which these and the earlier results of one of us and his collaborators has excited.

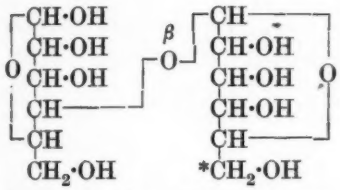
Chief among these criticisms have been those of Irvine in earlier papers (J., 1926, 867, 1506), but his more mature views appear to be concentrated in his recent article in *Chemical Reviews* (*loc. cit.*). The following extract from this article may be quoted : " In the structural classification of the disaccharides built up by Haworth " " this important issue * has been entirely overlooked," and " in addition, it is now recognised that his work involves a fundamental experimental error which renders his whole scheme valueless and that consequently, so far as the constitution of the disaccharides is concerned, we are only at the beginning of things in place of at the end."

Whilst affirming this belief, Irvine then proceeds to " turn to

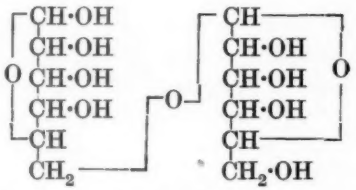
* Far from having been overlooked, this issue originated in a clear, cautious statement by one of us (J., 1926, 98, footnote) and it was there considered to be a possible though unlikely contingency, a view since justified in that it has been shown not to arise in any of the cases for which it was entertained.—W. N. Haworth.

the authentic results obtained," but instead of giving here only examples initiated by his own experimental work he quotes in detail, in the cases of no fewer than four of the six disaccharides, the experimental results and formulæ copied from our original papers published before he gave his address to the American Chemical Society (see *Chemical Reviews*), and in so doing he suppresses all reference and acknowledgment to the original authors.

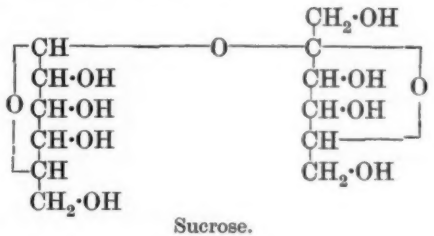
Irvine is committed to the advocacy of all but two of the constitutional formulæ for disaccharides initiated by one of us. The following are the formulæ quoted by Irvine in detail; these conclusions are identical with those previously given by Haworth and Hirst (J., 1921, **119**, 193), Haworth and Leitch (J., 1918, **113**, 188), Haworth and Wylam (J., 1923, **123**, 3120), Charlton, Haworth, and Peat (J., 1926, 89), and Haworth and Hirst (J., 1926, 1858).



Cellobiose (when both hexoses are glucose).
Lactose (when the hexose * is galactose).



Gentiobiose.



Sucrose.

The allocation of the above formula to sucrose was dependent upon, and could only have been made simultaneously with, the disproof and abandonment of Irvine's butylene oxide formula for normal fructose derivatives, since it is this formula which Haworth and Hirst then assigned (July, 1926) to the γ-fructose component in sucrose (compare subsequent paper by Avery, Haworth, and Hirst, this vol., p. 2308).

For the constitutions of the remaining two disaccharides, maltose and melibiose, against which the main criticism is evidently directed, Irvine has contended for the expressions (I) and (II) quoted already on p. 3146. The purport of the present communication is to demonstrate that in these two examples Irvine's formulæ are

erroneous, as is also his formula for raffinose, and it thus appears that in none of the six cases has a disaccharide formula been initiated by Irvine which has survived. The latter author has assigned, however, structural formulæ to cello*iso*biose and to the *iso*maltose of starch, although no experimental evidence accompanies these views and most workers, including the discoverers of these bioses, would do little more at this stage than postulate the probable existence of these two disaccharides (compare Haworth, *J. Soc. Chem. Ind.*, 1927, **46**, 295).

Experimental.

Oxidation of Melibiose to Melibionic Acid.—Melibiose (28 g.) having the recognised constants and having been prepared from pure raffinose was agitated with 210 c.c. of water to which were added in portions at intervals 16 c.c. of bromine, and the mixture was kept at about 20° with frequent agitation during about 7 days; then it appeared no longer to reduce Fehling's solution. The solution was then aerated, treated with hydrogen sulphide, and again aerated. Powdered litharge (50 g.) was added, and the mixture shaken for 4 hours until all the mineral acid present had been neutralised. The filtrate and the washings from the lead salts were shaken with finely divided silver oxide and the mixture was kept in the dark for some time. It was then filtered, treated with hydrogen sulphide, and again filtered, and the filtrate was evaporated and digested with precipitated calcium carbonate (10 g.). The filtrate and washings from this treatment were treated with charcoal and evaporated to a volume of 50 c.c. This solution was poured slowly with stirring into about 2 litres of methylated spirit. The precipitated, slightly glutinous solid was placed in contact with fresh methylated spirit and stirred until a hard granular product was formed. This was collected and dried in a vacuum, appearing as an almost white powder which was calcium melibionate. A further quantity of this calcium salt was recovered from the methylated spirit by evaporation, and purified as before by pouring into a fresh lot of methylated spirit. The dried calcium salt was devoid of action towards Fehling's solution. Yield, 92%. The calcium estimation showed Ca 4·74%. It thus appeared that the solid contained either two or three mols. of ethyl alcohol.

Methylation. Calcium melibionate (20 g.) was methylated in the usual manner with methyl sulphate in presence of sodium hydroxide, and the product was submitted to two similar treatments. The methylation process was completed by the use of Purdie's reagents, which were employed initially in presence of

a little water and finally the dry reagents were employed. The crude product resulting from this treatment contained OMe, 53·9%. It was then distilled under 0·05 mm., and the small amount (1·4 g.) of distillate collected below a bath temperature of 190° was rejected. The remaining portion of the distillate (12·5 g.) was collected at a bath temperature of 200—210°, and this on redistillation had b. p. 173 –175°/0·06 mm.; $n_D^{14°}$ 1·4640; $[\alpha]_D^{18°}$ + 106·4° in water (c = 1·63) (Found: C, 51·9; H, 8·5; OMe, 54·5. $C_{21}H_{40}O_{12}$ requires C, 52·1; H, 8·3; OMe, 57·65%). The product thus appeared to be essentially methyl octamethylmelibionate.

Hydrolysis. The above product was digested in a bath at 90° with a 7% solution of hydrochloric acid, and polarimetric readings were taken during the process of hydrolysis. The observations were taken by interrupting the course of the hydrolysis, removing a small sample and cooling, and these observations were continued until a constant rotation was obtained. $[\alpha]_D^{20°}$ + 106·1° (initial), 99·6° (after 30 mins.), 89·6° (60 mins.), 81° (90 mins.), 73·4° (120 mins.), 64·0° (180 mins.). After the solution had been kept overnight, the reading was + 64·3°, and it was ascertained that this reading remained constant after further heating. The mineral acid was then neutralised with barium carbonate, air being drawn through the solution at 50° to assist the neutralisation. The faintly coloured filtrate was treated with charcoal until quite colourless and evaporated at 40° in a vacuum. The residue was thoroughly dried by mixing it with acetone and removal of solvent, and finally by heating in a vacuum; the white residue thus obtained was extracted many times with boiling ether. The collected extracts yielded a syrup which crystallised on keeping. It was ascertained that this was 2 : 3 : 4 : 6-tetramethyl galactose (yield, 96·2% of the theoretical). The crystals were drained on porous tile and purified from light petroleum; m. p. 71—72°; $[\alpha]_D^{21°}$ + 117·8° (equilibrium). A mixed m. p. determination with an authentic specimen of 2 : 3 : 4 : 6-tetramethyl galactose proved its identity.

Again, 1 g. of the crude sugar was heated with 3 c.c. of aniline and 30 c.c. of ethyl alcohol during 5 hours. The crystalline tetramethyl galactose anilide separated and was recrystallised from ethyl acetate (yield, 92%); m. p. 192—193°, mixed m. p. determination with an authentic specimen prepared from lactose, 192—193°.

The residue remaining after the ether extraction of the tetramethyl galactose contained a barium salt of an organic acid. This was dissolved in water and treated with the equivalent of dilute hydrochloric acid to liberate the whole of the organic acid. The solution was completely evaporated at 30° in a vacuum and finally

at 35—40°. The residue was thoroughly dried by adding acetone and evaporating the solvent and finally by heating in a high vacuum at 70°. It was then extracted repeatedly with ether and the collected extracts were evaporated, yielding 4·2 g. of a tetramethyl gluconic acid (yield, 86·8% of the theoretical). The latter distilled under 0·05 mm. very slowly from a bath at 164°, giving a colourless, highly viscid syrup, which gave analytical figures pointing to its having been converted during this operation into an anhydro-form by condensation of two molecules (Found: C, 49·5; H, 8·0; OMe, 48·6. $C_{20}H_{38}O_{13}$ requires C, 49·4; H, 7·8; OMe, 51·0%).

The above undistilled acid (1 g.) was now oxidised in contact with 10 c.c. of nitric acid (*d* 1·2). Nitrous fumes began to be evolved at 75°. The temperature was gradually raised to 100°, and the solution maintained at this temperature for 5 hours. On removal of the nitric acid in a vacuum by repeated evaporation, accompanied by the intermittent addition of water, a liquid acid product was obtained. This was esterified with methyl-alcoholic hydrogen chloride (3%). Removal of the mineral acid was effected with silver carbonate and the filtrate was treated with charcoal to eliminate colloidal silver. A colourless liquid product (0·95 g.) was obtained on evaporation of this solvent. This was distilled under 0·09 mm. from a bath heated at 116—119°, and gave 0·8 g. of a colourless mobile liquid which crystallised during the distillation. This solid was recrystallised from dry ether, in which it was very soluble, giving hexagonal prisms, m. p. 77—78°. These were identical with the crystalline methyl tetramethylsaccharate which was prepared for the purpose of comparison by the methylation of saccharic acid. Karrer and Peyer (*Helv. Chim. Acta*, 1922, **5**, 577) also have prepared methyl tetramethylsaccharate from saccharic acid and they give m. p. 68°. By repeating the preparation of these authors, we also observed m. p. 68—71° for the partly purified material, but after three recrystallisations from ether the m. p. was raised to 76—77°. This preparation of the ester and of its derivatives will be described in a subsequent paper by Haworth and Jones. Mixed m. p. determination with the specimen isolated *via* melibiose, 77—78° (Found: C, 49·1; H, 7·2; OMe, 63·5. $C_{12}H_{22}O_8$ requires C, 49·0; H, 7·5; OMe, 63·3%). The diamide was also prepared: hexagonal plates (from water), m. p. 237—239° (Found: C, 45·4; H, 7·7; N, 10·7. Calc.: C, 45·4; H, 7·65; N, 10·6%).

The tetramethyl gluconic acid isolated as a cleavage product of methyl octamethylmelibionate is thus seen to be 2 : 3 : 4 : 5-tetramethyl gluconic acid, since it gives the tetramethylsaccharic acid on oxidation of a terminal $-CH_2\cdot OH$ group.

The authors express their gratitude to the Department of Scientific and Industrial Research for the award of a maintenance grant to one of them.

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[*Received, November 17th,* 1927.]

CCCCXIV.—*Ionisation and Chemical Change during Slow Combustion.*

By JAMES ALLAN JAMIESON BENNETT and ERNEST WALTER JOHN MARDLES.

DURING the period of slow combustion, important changes occur in a gas mixture rendering it sensitive to inflammation. Bone, Fraser, and Witt have recently demonstrated (*Proc. Roy. Soc.*, 1927, *A*, **114**, 442) that with mixtures of methane and oxygen when an electric spark is passed there is a definite lag or induction period before main combustion occurs. Ionisation has sometimes been detected during the slow combustion of a hydrocarbon, alcohol, etc., in air, and is associated with the formation of a fine mist (Bennett, *Trans. Faraday Soc.*, 1927, **23**, 295).

It has been found that a system containing liquid droplets is more ionised and more sensitive to ignition than the corresponding vapour mixture. Many different mixtures of *n*-hexane and air have been passed through a horizontal glass tube, heated in an electric furnace to 675°, without ignition occurring, but if the tube was tilted or held vertically, a fine mist passed back against the stream and then ignition often occurred as low as 550°. When hexane was sprayed down the tube ignition occurred at 570°. A similar behaviour was observed with a number of substances, as shown in Table I. The apparatus employed was the same as described by Callendar (*Engineering*, 1927, **123**, 147) and Bennett (*loc. cit.*); and the spontaneous ignition temperature given is the minimum observed on varying the mixture strength. The rate of flow through the tubes was the same for both spray and vapour.

TABLE I.

Spontaneous ignition temperatures of vapour or spray of some liquids in air; heated-tube method.

Substance.	Spray.	Vapour.
m-Xylene	610°	710°
n-Butyl alcohol	635	725
Undecane (b. p. 198—208°)	506	550
Benzyl alcohol	546	571
Amyl ether	516	591
Cymene (b. p. 174—176°)	571	606

The minimum ignition temperature obtained with a falling temperature was often much lower than with a rising temperature. Thus, with a mixture of acetylene and air a sharp explosion first occurred at 340° with a rising temperature, but on lowering the temperature the mixture continued to catch fire at intervals even below 300° without violence, indicating that something remained in the tube from the previous combustion which rendered the fresh gas mixture sensitive to ignition.

Chemical changes occur below the ignition temperature, and these were usually more marked and occurred at lower temperatures with the liquid drops present than with the vapours alone. Thus with cymene at 370° the aldehyde and peroxide tests were given by the liquid drops but not by the vapour; lime-water was turned milky at 425° by the products from the spray, but it was necessary to raise the temperature to 440° in the case of the vapour before the presence of carbon dioxide could be definitely demonstrated. Table II gives some results obtained with a spray in quartz tubes with light from the mercury-vapour lamp. The electrical conductivity was measured in the manner described by Bennett (*loc. cit.*).

TABLE II.

Chemical and ionisation changes during the slow combustion of (*a*) cymene; (*b*) amyl ether; (*c*) undecane.

	Temp.	Observations.
(*a*)	275°	Aldehyde and peroxide tests given.
	300	Fog formed; slight ionisation.
	400	Dense, white fog, with pronounced ionisation; carbon dioxide present.
(*b*)	120	Aldehyde and peroxide tests given.
	300	Slight ionisation; white fog formed.
(*c*)	150	Aldehyde and peroxide tests given.
	275	Slight ionisation; white fog formed.
	450	Pronounced ionisation; dense white fog and nearly complete combustion of undecane to aldehydes, acids, CO_2, etc.

Although the high degree of ionisation is regarded as an accompaniment of, rather than as the direct cause of, detonation in the internal-combustion engine (Symposium on Gaseous Reactions, *Trans. Faraday Soc.*, October, 1926), yet the important rôle that can be played by electron emission follows from Callendar's nuclear-drop theory, the electron being capable of acting as a nucleus (Aeronautical Research Committee, R. and M. 1013, H.M.S.O.).

The coincidence of mist formation and ionisation during the slow combustion of a large number of substances raised the question as to whether ionisation was due to the development of surface (compare Simpson, *Phil. Trans.*, 1909, *A*, **209**, 379) or whether it was

the result of chemical change, and this matter is under investigation.

Although it is not certain whether all gaseous reactions are accompanied by ionisation (compare Trautz and Henglein, *Z. anorg. Chem.*, 1920, **110**, 257), the results shown in Table III indicate that at higher temperatures slight ionisation occurs with some mixtures. Moreover, Brewer (*Proc. Nat. Acad. Sci.*, 1926, **12**, 560) has observed ionisation during the catalytic oxidation of a number of organic substances, *e.g.*, xylene, acetone, etc.

TABLE III.

Mixture with air.	Composition (% by vol.).	Temp. of initial combustion.	Temp. when slight ionisation first observed.
Carbon monoxide	48·5	465°	500°
" "	9·0	460	460
Carbon monoxide and hydrogen	{ 22% CO / 11% H_2 }	430	430
Hexane	5	350	650
Ethyl ether	10	173	400

In no case was ionisation observed below the temperature of initial oxidation, *i.e.*, when aldehydes were first detected, and usually only slight ionisation was observed at higher temperatures even when oxidation was extensive. This delay might appear to throw some light on the mechanism of chemical reaction during the combustion of hydrocarbons. The scission of the oxygen molecule into atoms would probably result in profuse liberation of electrons so that hypotheses of oxidation and combustion at moderate temperatures which involve this atomic separation (*e.g.*, the hydroxylation theory) are not so convincing as those in which the oxygen molecule is regarded as being incorporated as a whole, *i.e.*, when O = O becomes — O — O — in the formation of peroxides from hydrocarbons:

$$R{\cdot}CH_3 + O_2 \rightarrow R{\cdot}CH_2{\cdot}O{\cdot}O{\cdot}H; \quad >C{:}C< + O_2 = >C\underset{O}{\overset{O}{-}}C<.$$

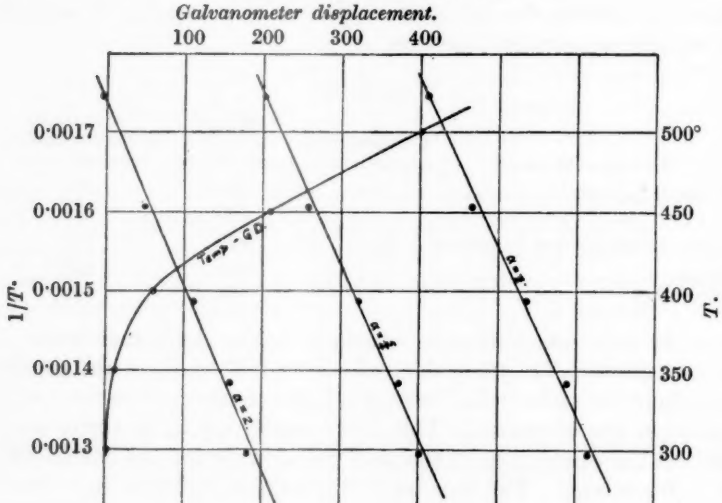
The formula $i = \theta T^{\alpha} e^{-\phi/T}$ (where $\alpha = \frac{1}{2}$, $\frac{5}{4}$, or 2; i = current; T = temperature; and θ and ϕ are constants) satisfies cases of thermionic emission, ionisation in flames, and ionisation in liquid drops–air systems during slow combustion, since in each case, within the limits of experimental error, all points plotted with axes (log $i - \alpha \log T$) and $1/T$ fall on straight lines (Bennett, *loc. cit.*).

The rate of chemical action, dc/dt, is expressed by the above equation if $\alpha = \frac{1}{2}$ and $i = dc/dt$. Richardson concluded that since ϕ in the case of chemical action differs from that in the case of thermionic emission the emission cannot be due to chemical action, but Brewer (*loc. cit.*) has now accounted for this difference.

In the light of these conclusions it seems probable that the pro-

cesses occurring at the beginning of and during combustion are (*a*) a thermionic emission and (*b*) the formation of centres of chemical change from ions as soon as they are liberated (compare Lind and Bardwell, *J. Amer. Chem. Soc.*, 1926, **48**, 2335).

FIG. 1.



Action of Iron Carbonyl, Lead Tetraethyl, Aniline, etc., on Slow Combustion and Ionisation.

The presence of iron carbonyl, lead tetraethyl, etc., even in small quantities exerts a great influence on slow combustion, delaying spontaneous inflammation and altering the temperature at which appreciable combustion begins. Some results are given in Tables IV and V.

TABLE IV.

The influence of lead tetraethyl and iron carbonyl on spontaneous ignition temperature.

Substance, spray in air.	Spontaneous ignition temp.
m-Xylene	610°
„ plus 0·3% (vol.) lead tetraethyl	650
„ „ 0·5% (vol.) lead tetraethyl	688
„ „ 1·0% (vol.) iron carbonyl	700
n-Butyl alcohol	635
„ „ plus 1% (vol.) lead tetraethyl	687

TABLE V.

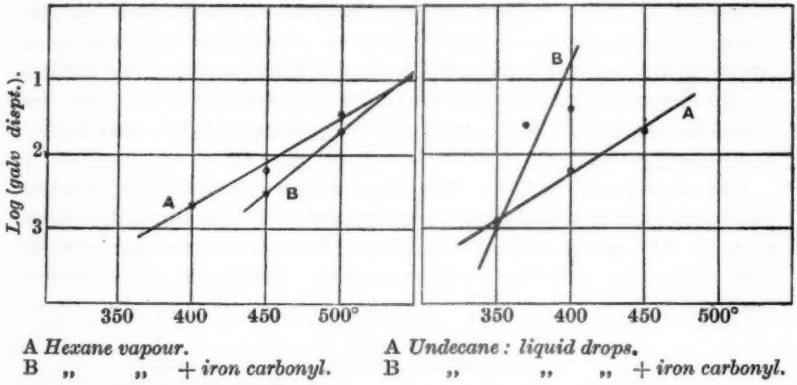
The influence of iron carbonyl, lead tetraethyl, etc., on chemical change and ionisation during slow combustion.

Substance.	Temp. of initial combustion.*	Ionisation.
Undecane, spray in air	200°	Very slight at 275°.
„ plus 0·2% iron carbonyl	238	Not detected until 330°.
„ „ 0·5% lead tetraethyl	305	Less than with undecane alone, below 350°.
„ „ 20% *m*-toluidine	248	The same as with undecane.
„ „ 20% *m*-xylidine	275	„ „ „
„ „ 20% *m*-cresol	310	Not detected until nearly 400°.
„ „ 20% carbon disulphide	230	„ „ „

* *I.e.*, as measured by the appearance of aldehydes.

The action of iron carbonyl, lead tetraethyl, and other "anti-knockers" appears to be the inhibition of peroxide formation during

FIG. 2.



A *Hexane vapour.*
B „ „ + *iron carbonyl.*

A *Undecane: liquid drops.*
B „ „ „ + *iron carbonyl.*

the period of slow combustion (Callendar, *loc. cit.*), and although below a temperature of about 400°, iron carbonyl and lead tetraethyl reduce the rate of chemical change, yet at higher temperatures there is a higher yield of water and carbon dioxide. This is shown in Table VI.

It will be seen from Fig. 2 that the ionisation curves for a very rich mixture of hexane and a spray of undecane containing iron carbonyl cross those for the "undoped" fuel, indicating that the initial decrease in chemical change is accompanied by a decrease in electron emission, whilst increased ionisation at higher temperature results from increased combustion, probably at the surface of the metal particles produced by the thermal decomposition of the metallic compounds.

TABLE VI.

The influence of lead tetraethyl on the quantity of carbon dioxide in the oxidation products of *n*-hexane at different temperatures.

	% CO_2 in oxidation products,	
Temp.	without lead tetraethyl.	with about 0·25% lead tetraethyl.
265°	Trace	Nil
300	2·1	Trace
400	1·9	3·3

Experiments with hydrogen, and with hydrogen–air, hexane–air, coal-gas–air, and acetylene–air mixtures, with and without puffs of iron carbonyl, lead tetraethyl, and nickel carbonyl, were made at temperatures up to 600°, and usually the addition of the organometallic compound was found not appreciably to increase ionisation. By a special device, only a trace of iron carbonyl, etc., was allowed to enter the stream of gases, and then only for a few seconds while the reading was being taken. With carbon monoxide–air mixtures there was a rapid movement on the galvanometer scale as the "doped" gas mixture passed across the electrodes, followed by a return to the normal reading after the puff had passed. The fouling of the electrodes and tube caused much difficulty in measuring the ionisation, and they had frequently to be thoroughly cleaned during the experiments.

The mixture (67% CO + 33% H_2)–air gave very striking results. As a puff rich in iron carbonyl was passed through the combustion tube at 500° along with the mixture, the current passing between the electrodes increased approximately 2000-fold. The actual readings were :

Temp.	Galvanometer displacement (mm.).	Remarks.
430°	3	Without $Fe(CO)_5$.
500	25	" "
500	450 (with shunt, 100)	With $Fe(CO)_5$.
500	35	After passage of puff.

It will be noticed that (1) after the puff had passed through the tube the conductivity decreased to its former order of magnitude, (2) there was a slight persistence of increased conductivity, (3) the galvanometer reading did not increase suddenly, but at first it moved gradually and then rapidly accelerated till, when the spot had reached the end of the scale, its velocity was very great. The state of ionisation tends to remain unchanged.

Some typical results with the less effective mixtures are given in Table VII.

A mixture of air and iron carbonyl was passed through the combustion tube and did not cause any movement of the galvanometer.

TABLE VII.

Mixture.	Strength of mixture.	Temp.	Galvanometer displacement (mm.).	Remarks.
CO plus air	Weak	520°	0	—
" "	"	600	2	—
" "	"	550	2	With lead tetraethyl.
" "	"	600	7	" " "
Hydrogen–air ...	Rich	(335—650)	0	—
Iron carbonyl ...	"	"	0	—
Hydrogen plus air	50%	(525—600)	0	—
" "	"	"	2	With lead tetraethyl.
" "	"	"	5	With iron carbonyl.
" "	10%	(450—570)	40	With lead tetraethyl.
Coal-gas–air	50%	610	10	—
" "	"	"	20	With iron carbonyl.
Acetylene–air ...	Weak	(150—470)	0	—
" " ...	"	470	1	With nickel carbonyl. On addition of iron carbonyl, temp. of electrodes rose suddenly to 800° and mixture exploded.
" " ...	"	500	—	

The addition of a puff of the hydrogen–carbon monoxide mixture increased the conductivity to a high degree, as described before. The temperature was not increased by the puff and it must therefore be concluded that the ionisation was due to chemical change.

The characteristic action of lead tetraethyl and iron pentacarbonyl on the slow combustion of the gases mentioned was to delay spontaneous ignition and to lower the temperature at which slow combustion began by 50—100°. However, at 600° the amount of oxidation of carbon monoxide was not appreciably affected by the presence of small amounts of these substances.

These investigations are published by permission of the Director of Scientific Research, Air Ministry.

AIR MINISTRY LABORATORY,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, S.W. 7.

[*Received, May 18th*, 1927.]

NOTES.

Pregl's Universal Filling applied to Macro-combustions. By WILLIAM DAVIES.

THE filling used in Pregl's method ("Die Quantitative Organische Mikroanalyse," 1923) of carbon and hydrogen determination has now been applied successfully on a macro-scale, and as such a universal filling has many advantages, the method is briefly indicated.

An ordinary combustion tube of about 1·2—1·5 cm. internal diameter and 95—100 cm. long is used. A plug of silver wool or silver gauze (1·5 cm.) precedes the filling of mixed copper oxide (wire form) and lead chromate (about 43 cm.); this is followed by a mixed

silver wool and asbestos plug (2·5 cm.), and finally by a filling of lead peroxide asbestos (about 13 cm.). The last is prepared after Pregl (*op. cit.*, p. 29), but the thorough drying of this material on a large scale offers some difficulties, for the temperature at which the peroxide begins to decompose is somewhat uncertain (100—290°; see Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. VII, p. 687); that used in these experiments was dried in bulk at 200° for 4 hours, then spread out in shallow vessels and dried for 8 hours over calcium chloride at 100° under less than 30 mm. pressure, and finally heated before use for 3 hours in a rapid stream of air in the combustion tube at 180°. Even after this treatment a trace of moisture was still left, and the first value for hydrogen with a new tube was apt to be slightly high. The lead peroxide in the combustion tube is heated by a hollow boiler (15 cm. long and with a hole of 2·5 cm. diameter) made of brazed copper and is modelled on Pregl's "Hohlgranate." The "Kupferbügel" is best in the form of an almost cylindrical piece of copper (5 cm. long) which practically surrounds the combustion tube and is connected round the middle to the copper boiler by means of a thick copper rod. The boiler requires about 50 c.c. of liquid, and technical *o*-dichlorobenzene, b. p. 177—181° (corr.), is used. The furnace end of the boiler is provided with an asbestos ring which fits closely round the combustion tube, and the portion of the combustion tube in the boiler is loosely packed with asbestos. (For the construction of these boilers the author is indebted to Mr. J. L. Osborne.)

Owing to the much larger contact surface presented by the macro- as compared with the micro-filling, the Mariotte flask adopted by Pregl is discarded. Soda–lime and calcium chloride are used both in the purifying train and in the absorption tubes. The combustion is carried out in the ordinary way, care being taken not to heat too strongly that portion of the furnace immediately before the copper boiler. The silver filling and lead peroxide asbestos suffice for about 10 combustions.

The method has been thoroughly tested for many types of substances, including those containing halogens and sulphur, and both amino- and nitro-groups; representative analyses for such substances are: Chlorobenzene-2 : 4 : 6-trisulphonyl chloride (Found: C, 17·7, 17·7, 17·5; H, 0·9, 0·7, 0·6. Calc.: C, 17·6; H, 0·5%). Acetanilide (Found: C, 70·9, 71·1; H, 6·6, 6·5. Calc.: C, 71·1; H, 6·7%). *p*-Chloronitrobenzene (Found: C, 45·6, 45·5, 45·5, 45·8; H, 2·5, 2·5, 2·4, 2·6. Calc.: C, 45·7; H, 2·5%). 2 : 4-Dinitrotoluene (Found: C, 46·2, 46·0, 45·9; H, 3·2, 3·4, 3·4. Calc.: C, 46·1; H, 3·3%). Picryl chloride (Found: C, 29·1, 28·9, 29·1; H, 1·2, 0·9, 0·9. Calc.: C, 29·15; H, 0·8%).—MELBOURNE UNIVERSITY. [*Received, September 19th*, 1927.]

The Electroendosmosis of Aqueous Solutions through Glass Diaphragms. By HORACE CHARLES HEPBURN.

FAIRBROTHER and VARLEY (this vol., p. 1584) have measured the electroendosmosis of dilute hydrochloric acid through a diaphragm of sintered Jena " Geräte " glass powder, and their results lead them to conclude with Lachs and Kronman (*Rocz. Chem.*, 1926, **6**, 641) that the interfacial equilibrium between glass and aqueous solutions is not a true one, but changes with time. They give the results of two series of electroendosmotic determinations with dilute hydrochloric acid, the second series consisting of a repetition of the first series after the diaphragm had been " carefully cleaned." In each series, the results were " quite concordant among themselves," but the electrokinetic potential was throughout less negative in Series II than in Series I. No reference is made to the lowering of electrokinetic potential produced by given concentrations of hydrochloric acid; when this factor is considered, however, the two series of results show a remarkable similarity. The lowering is given by $\zeta_0 - \zeta_c$, where ζ_0 and ζ_c represent the electrokinetic potential at concentrations zero and c, respectively; and values for $\zeta_0 - \zeta_c$, obtained from Fairbrother and Varley's results, are given in the subjoined table. It will be observed that, except in the case of the most dilute solution (where the potential lowering is small and the value is affected to a greater extent by experimental error), the two series of values are in satisfactory agreement.

	Lowering of electrokinetic potential (volt).	
Solution.	Series I.	Series II.
N/5000-HCl	0·0041	0·0075
N/1250-HCl	0·0113	0·0111
N/400-HCl	0·0163	0·0169
N/100-HCl	0·0310	0·0309

Thus, contrary to the view of Fairbrother and Varley, there appears to be little indication from these results of any change in the effective size of the diaphragm pores corresponding to a progressive swelling process at the glass surface; on the other hand, it seems probable that these authors, in the process of cleaning their diaphragm, failed to remove the last traces of adsorbed electrolyte. The difficulty in bringing a diaphragm back to its original state after treatment with an electrolyte solution has been referred to by Freundlich and von Elissafoff (*Z. physikal. Chem.*, 1912, **79**, 385), who found, in some instances, that repeated treatment with concentrated nitric acid was necessary; similar treatment of a diaphragm of powdered glass, however, introduces the difficulty of removing the final traces of acid by washing with water. Fairbrother and Varley were able to reproduce the value of ζ obtained in the initial determination with water by treating the diaphragm

with nitric acid, but subsequent determinations with dilute hydrochloric acid gave results deviating from the original values.

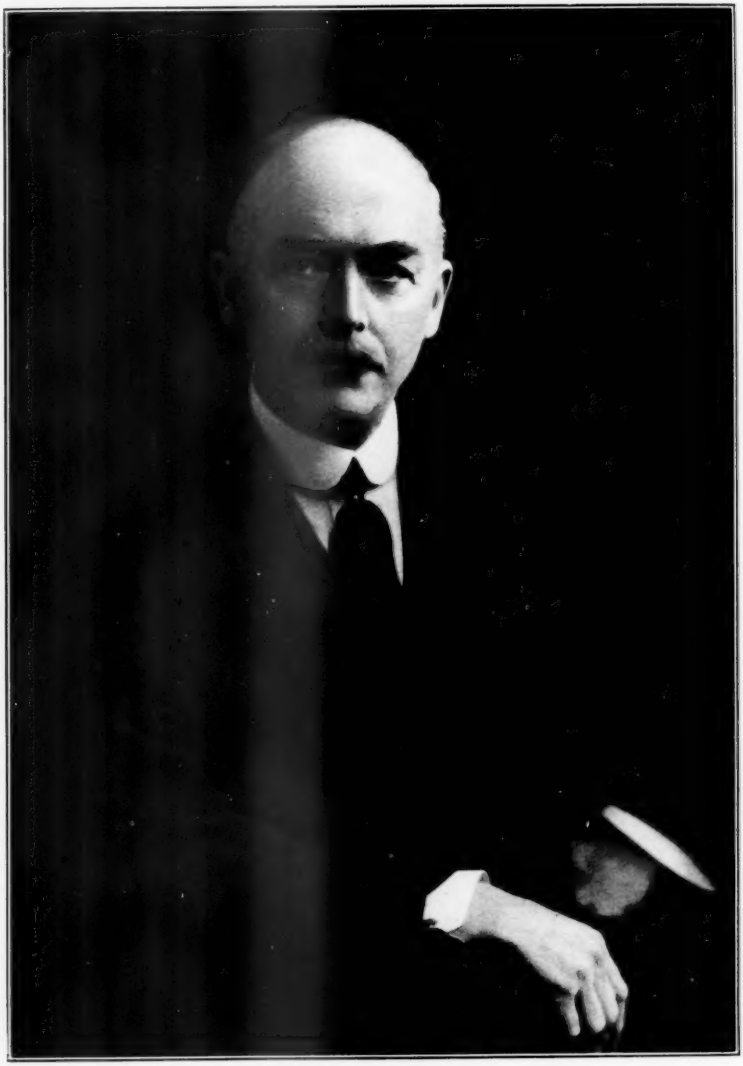
The author (*Proc. Physical Soc.*, 1926, **38**, 363; 1927, **39**, 99) has surmounted the difficulty in bringing a diaphragm back to its original state after treatment with an electrolyte solution by employing an entirely fresh diaphragm for each series of observations. When this procedure was followed, it was possible to obtain concordant results in determinations made at intervals over a period of several months.—BIRKBECK COLLEGE (UNIVERSITY OF LONDON). [*Received, September 2nd*, 1927.]

The Use of Hydrogen Peroxide for Iodine and Other Substitutions in Aromatic Compounds. By JAMES ERNEST MARSH.

HYDROGEN peroxide may be used to facilitate substitutions. For example, a solution of phenol in alcohol with the calculated quantity of iodine is warmed and hydrogen peroxide (30%) is added, the colour of the iodine gradually disappears, and 2 : 4 : 6-tri-iodophenol crystallises. Similarly β-naphthol yields 1-iodo-β-naphthol in quantitative amount.

It is not necessary to start with iodine in the free state. When phenol is dissolved in glacial acetic acid, the requisite amount of potassium iodide added, and the solution heated, the addition of hydrogen peroxide brings about the quantitative separation of tri-iodophenol; replacement of the potassium iodide by a metallic bromide gives tribromophenol, and replacement by hydrochloric acid gives trichlorophenol.

The thiocarbimido-group can be introduced as follows: Dimethylaniline and potassium thiocyanate in molecular proportion are dissolved in glacial acetic acid and hydrogen peroxide is added gradually. The solution becomes hot and, on cooling, the compound $C_9H_{10}N_2S$ crystallises. It may be recrystallised from alcohol and forms colourless plates, m. p. 73° (Found: C, 61·0; H, 5·7; N, 15·7; S, 18·3. Calc.: C, 60·6; H, 5·6; N, 15·7; S, 18·0%). This compound was obtained by Söderbäck (*Annalen*, 1919, **419**, 275) by the action of an ethereal solution of thiocyanogen on dimethylaniline. It is probable that it is not a simple thiocyanogen derivative of dimethylaniline, but that it is identical with the compound which Schmidt synthesised (*Ber.*, 1906, **39**, 2409) by the action of nitrous acid on the condensation product of formaldehyde with *as*-dimethyl-*p*-phenylenediaminethiosulphonic acid, and to which he assigned the constitution $NMe_2 \cdot C_6H_3 < \begin{matrix} S \\ N \end{matrix} > CH$.—UNIVERSITY MUSEUM, OXFORD. [*Received, October 28th*, 1927.]



A. W. CROSSLEY.

[*To face p.* 3165.]

OBITUARY NOTICES.

ARTHUR WILLIAM CROSSLEY.

BORN FEBRUARY 25TH 1869: DIED MARCH 5TH 1927.

ARTHUR WILLIAM CROSSLEY was born at Bentcliffe, Accrington, on February 25th 1869. His father, Richard Crossley, was a man of unusual qualities who after returning from America with ample means and losing the greater part, moved into Accrington in 1864 to make what amounted almost to a fresh start as manager to the firm of F. W. Grafton & Co., well known as calico printers. If Crossley owed his quiet, reserved disposition to his father, his tenacity and resolution were inherited from his mother, a Bissett of Aberdeen and a woman of remarkable energy and force of character. Of his boyhood little of interest can be recalled: it seems to have been uneventful and happy. From preparatory school he went in 1881 to Mill Hill—chosen for its nonconformist tradition—where he stayed until Easter 1885. The next three months were spent in Paris. In the following October he entered Owens College, but owing to an illness which caused the loss of a year, he did not obtain his Honours degree of B.Sc. until 1890.

After a session spent in Professor (now Sir Arthur) Schuster's laboratory, which led to the joint publication of a paper on the electro-deposition of silver (*Proc. Roy. Soc.*, 1892, **50**, 344), Crossley went to Emil Fischer at Würzburg in October 1891, stayed there until Fischer was translated to Berlin in succession to A. W. von Hofmann in the autumn of 1892 and remained with him in Berlin until the Christmas of that year. Before leaving Würzburg the degree of Ph.D. was conferred on him for his thesis entitled "I., Ueber die Oxydation einiger Dicarbonsaüren; II., Ueber das optische Verhalten des Dulcits und seiner Derivate."

Returning to Owens College early in 1893 to undertake research work with W. H. Perkin, junr., he was elected to a Bishop Berkeley research fellowship in the following year and became President of the College Union, revealing in the conduct of its affairs thoroughness and a sanity of judgment that later came to be recognised as characteristic. This admittedly was one of the happiest periods of his

life: he widened his social circle, was an active member of many college societies and, freed at last from the tyranny of examinations, gave regular hours to the cultivation of his singing voice—a baritone of fine quality and wide range. But for its uncertainty, he might have chosen the concert platform as a career rather than chemistry which, until devotion to experimental work came to possess him, was more his father's choice than his own. In April 1895 he was appointed teacher and demonstrator in physics and chemistry at St. Thomas's Hospital Medical School, where he succeeded Professor (now Sir Wyndham) Dunstan as chemical lecturer and consulting chemist in October 1900. Four years later he became Professor of Chemistry at the Pharmaceutical Society's School of Pharmacy, Bloomsbury Square. As the outcome of Crossley's research work at Owens College, two papers were published jointly with Perkin, the first in 1894 under the title "Substituted pimelic acids," (J., **65**, 987) and the second in 1898, nearly three years after his departure from Manchester, entitled "Decomposition of camphoric acid by fusion with potash or soda," (J., **73**, 1). Dihydrocamphoric acid, one of the products mentioned in the second paper, was the starting point of the series of investigations which occupied his attention until the outbreak of the War and led to the publication of some 40 papers in the Journal. With some of the early communications from St. Thomas's Hospital, the late Dr. H. R. Le Sueur was associated and in many of those from the School of Pharmacy, Miss Nora Renouf was his collaborator.

The earliest papers of the series dealt with attempts to synthesise $\alpha\alpha_1\beta\beta$-tetramethyladipic acid on the assumption that dihydrocamphoric acid had that constitution. Of the intermediates examined, 1 : 1 : 2-trimethyldihydroresorcin, obtained for the purpose by the condensation of mesityl oxide and ethyl sodiomethylmalonate, and 1 : 1-dimethyldihydroresorcin, its lower homologue, which had been made slightly earlier by Vorländer, proved so unexpectedly reactive that the original quest was abandoned. In its place, the detailed study of these hydroaromatic compounds and of their reduction, halogen and ketonic derivatives was pursued with ardour, leading as it did to the production of *o*-xylene derivatives by the migration of one of the members of the *gem*-dimethy group.

In the papers many indications of the care taken to check the occurrence and course of these transformations can be found. These led incidentally to the production of mono-, di- and tri-nitro-*o*-xylenes and to the preparation of all the isomeric forms of these substances. Further, a contribution to the loosening effect of nitro-groups

situated in the *ortho*- or *para*-position relatively to a given nitro-group arose out of the conversion of certain trinitro-*o*-xylenes into dinitro-*o*-xylidines by interaction with ammonia. And the emergence of halogenated *o*-xylenols in the later stages of the investigation showed the interest of the subject to be far from exhausted, when the War brought the work to an end.

Much attention was paid to the exact characterisation of hydrocarbons of the di-, tetra- and hexa-hydrobenzene series isolated in the course of the work, as troublesome obstacles were encountered owing to the frequent occurrence of mixtures of isomerides, closely similar in properties, in the synthetical products. As serving to connect these products with camphor and the terpenes, the synthesis of *iso*laurolene and of *cyclo*geraniolene may be noted. From the manner in which each experimental difficulty was attacked and solved, the whole investigation affords a good example of the art of scientific discovery.

It was especially during his tenure of the Chair at the School of Pharmacy, which lasted from 1904 to 1914, that Crossley found scope for the exercise of those qualities of organisation, tact and driving power which later were to be of inestimable service to the State. To him fell the completion of the scheme initiated by his predecessor for remodelling and re-equipping the Chemistry Department, aided as he was by the cordial co-operation of the veteran Michael Carteighe who, far-seeing and insistent, laboured to the end of his life for the advancement of the scientific side of pharmacy.

In his inaugural address at Bloomsbury Square, Crossley made it clear to the students that in his view pharmacy is "a great applied science" and also "a great profession" (*Pharm. J.*, 1904, **73**, 497). Imbued with this conception of the dignity of their calling, he set them a high standard of duty by the conscientious performance of his work as professor. No external interest, not even the fascination of research, was allowed to interfere with his weekly tour of the laboratory or that personal contact with each student to which he attached the utmost importance. But it was in his research laboratory—a curious, octagonal room, by no means well lighted or equipped for advanced work—that his devotion to chemistry found its outlet. There, too, by his example he inculcated thoroughness, careful observation and an ordered use of all laboratory hours, and, always open to suggestions or ideas from his fellow workers, he never failed to show appreciation of their share in bringing a research to a successful conclusion.

Naturally, all through this period, Crossley looked to a University Chair as his ultimate aim. When, therefore, he was appointed

Professor of Organic Chemistry in King's College, London, in June 1914, the wider opportunities for teaching and research that he coveted seemed at length to be his. But Fate willed otherwise. Within little more than a month, the Great War broke out and—save that he gave lectures during the session 1914/15 and returned to the College for a few months after the Armistice—his work as a Professor was done. Henceforward his energies were to be absorbed first in the country's defence and later in the effort for reconstructing industry that has followed the Peace.

Never one to wait, in an emergency, for employment fitting his attainments, Crossley in the earliest days of the War cheerfully undertook arduous clerical work as a volunteer in the War Office under Colonel (now Sir John) Pringle who was engaged in organising railway transport for troops in the Home Defence, Eastern Command and London District areas. Then, after aiding in the large-scale production of salvarsan under the name kharsivan, he became secretary of the War Committee appointed by the Royal Society to organise the production in universities and kindred institutions of local anaesthetics such as novocaine and β-eucaine and of other drugs hitherto obtainable only from enemy sources.

The bitter cry for shell in the spring of 1915 led to the establishment of the Ministry of Munitions. Of its Departments, that dealing with Trench warfare had for one of its functions the provision of all material required for the offensive in chemical warfare, rendered necessary by the introduction of gas as a weapon by the Germans on the western front on April 22nd of that year. As part of the organisation, two Committees termed Scientific Advisory and Commercial Advisory were set up in June * and of each Crossley was appointed secretary. The early days of chemical warfare were for him full of anxiety and incessant toil. The Scientific Advisory Committee sat almost continuously during each day; at night steps had to be taken to carry into effect its decisions. Crossley, as secretary, stood between the military in urgent need of new weapons the nature of which, perforce, they could not describe, and the Advisory Committee, faced with utterly new problems vitally important but requiring time, of which there was all too little, for their solution. In these early days, the contact between those in the fighting line and those working at home to provide the sorely-needed chemical weapons was small. To enable the latter to form some conception of the conditions at the front, Crossley was

* The Scientific Advisory Committee was a body of distinguished scientists charged with the duty of devising and investigating methods of prosecuting chemical warfare, the Commercial Advisory Committee a group of leading men in the British Chemical Industry in a position to advise upon and assist in the production of the necessary chemical materials.

given the additional appointment of Liaison Officer for Chemical Warfare in November 1915 with the rank of Lieutenant-Colonel and in this capacity made several visits to the battle areas in France.

Only slowly did the authorities at home realise that for the successful development of chemical warfare it was essential there should be available a large experimental ground where trials could be carried out on a scale approaching that of actual warfare. Space was required for testing under varying meteorological conditions both the methods of producing and the lethal or visual effects of toxic " gases " and smokes distributed from cylinders, by artillery fire, or otherwise. Eventually a large tract of bare land was acquired at Porton, east of Salisbury, and to Crossley in June 1916 was entrusted the task of converting it into a suitable experimental ground, of staffing and equipping it and of supervising the experimental work undertaken at the instance of the Army or the Committee. Thereupon, he ceased to be secretary of the Committee,* but was retained as a member and also as liaison officer.

How great the difficulties were and how he overcame them may be understood at least in part from the following appreciation most kindly furnished by Lieutenant-Colonel (then Major) R. M. Rendel, R.A., a regular officer who served under Crossley for two years—for the first three months as his adjutant and afterwards as one of his experimental officers.

" When Crossley arrived at Porton he found two small Army huts, each 30 feet by 15 feet, in the middle of Salisbury Plain, with no roads leading to them, no water, and no equipment of any kind. He was, with the exception of one subaltern R.E. and one warrant officer, quite alone. His first move was to get himself appointed to the military command of the Experimental Station; his second to collect the nucleus of a staff. By the end of June he had a chemical laboratory running in one of his Army huts, and by the end of the year detachments of Artillery and Engineers under their own officers had been posted to the Station. He was now in a position to begin the preliminary experiments, which were necessary for the solution of the hundreds of questions that had to be answered before the British Armies in the field could undertake chemical warfare.

" It would take too long to sum up the work done by Crossley

* The Scientific Advisory Committee was modified and re-named in successive reorganisations. Eventually it became the Chemical Warfare Committee, a body of enlarged constitution responsible for scientific investigations on the defensive as well as the offensive side of chemical warfare. Throughout its transformation and afterwards, Crossley continued to be a leading member.

during his two and a half years at Porton. It is doubtful whether anyone realises the immense volume of work actually achieved. Crossley himself wrote a summary for the War Records, a copy of which is filed at Porton, but it is both much too long and much too official to reproduce here. It may be of interest, however, to consider that at the time of the Armistice, little over two years after the beginning of the Experimental Station, Porton was staffed by 47 officers, 700 N.C.O.'s and men and 800 civilian workmen. Of the 47 officers roughly half were trained scientists, principally chemists and physiologists, several of them very eminent men. The two original Army huts had been replaced by large laboratories, workshops, gunsheds, magazines, barracks and canteens. Permanent roads were in existence over the ground; telephones, electric light, and water had been laid on. Large stores of shell, gas and so on, were situated on the ground and about 40 pieces of ordnance of all natures, from 9·2 howitzers downwards, and trench mortars of every description, were under Crossley's command. Over 40,000 rounds of ammunition had been fired, thousands of experiments had taken place and some of the results of Crossley's work had been embodied in over 800 reports. Chemical warfare was already highly developed.

"During those two years or more, from the moment Crossley came to the Station, work was carried on all day and during most of the night. Such was his driving power that lack of facilities never seemed to matter. It was one of Crossley's outstanding merits that, although he himself fully realised the difficulty of working without proper tools, yet he never allowed the lack of them to become an excuse for doing no work.

"Apart from the fact that it was wartime, work at Porton was carried on in a very pleasant atmosphere. There were no jealousies or bickerings between those engaged on the experiments. Whatever the differences of opinion between individuals, once a report had been issued it was always accepted as the official Porton view. It was always signed by Crossley, unless it were purely physiological, so that the Station did actually achieve an entity of its own. If reference were made to Porton, whether as regards some chemical question or as regards the functioning of a particular fuze, the reply was the Porton reply, the opinion the Porton opinion, the work was the work of Porton and Crossley signed the report. The physiologist was proud of the work done by the chemist, the chemist recognised the achievements of the gunner. A most valuable corporate feeling was thus created; it was entirely due to Crossley, and it was only possible because, while he always took responsibility for all that was said or done, he never took to himself credit

which was really due to others. All his staff were well aware of this.

"His position as commanding officer was a very real one. He was in actual military command of nearly 1,000 men, almost every one of whom had more military experience than he had. The type of man serving at Porton during the War was very good, but it is certainly to the credit of Crossley that serious military crime, both during the War and after the Armistice, was non-existent at Porton.

"He was the most hardworking of men. Sometimes severe, he very seldom praised; but he was absolutely fair-minded and all the time he was at Porton I never heard him criticised by any one of his staff. We were all devoted to him. Crossley was the best Commanding Officer I ever served under."

In September 1918, Crossley was appointed Daniell Professor of Chemistry and Director of the Chemical laboratories in King's College on the resignation of Sir Herbert Jackson, and after demobilisation returned to the college in October 1919. In common with many of those engaged in the big enterprises of the War, he found the routine of post-war days irksome, although with undiminished vigour he set himself to rebuild his department and revive academic research under the difficult conditions then prevailing. Soon the call came to him to undertake the organisation of the British Cotton Industry Research Association founded by the Lancashire cotton trade with the co-operation of the Department of Scientific and Industrial Research. Appointed Director on November 4th 1919, and leaving King's College in March 1920, it was on his recommendation that the house at Didsbury, now known as the Shirley Institute, was purchased. While it was being adapted to its new use and extended by the erection of a large block of laboratories and workshops, a beginning was made with cotton research in laboratories lent for the purpose by the University and by the Technical College in Manchester. To the Institute, the research staff was transferred early in 1922, the buildings being opened formally by H.R.H. the Duke of York on March 28th of that year. By the autumn of 1926, the research staff (including those of its members engaged in the workshops) which in 1921 numbered 28, had increased to 92 of whom 44 were university graduates. An account of some of the investigations in progress at the Institute formed the subject of a discourse given under the title "Science and the Cotton Industry," by the Director at the Royal Institution on Friday, January 23rd 1925.

In the autumn of 1923, the initial period of association with the Department of Scientific and Industrial Research drew to its close, and, although little more than a year of normal working had been

possible, the results were sufficiently encouraging to warrant a further grant of £45,000, spread over five years in a series of diminishing amounts, being made by the Department, on condition that the total annual income was raised to a minimum of £42,500. It was a source of much satisfaction to Crossley, and an unmistakable proof of confidence in his directorship that an industry hard hit as the cotton trade has been since the Peace, should shoulder the additional burden imposed by this condition. His aim was to make the Shirley Institute the brain of the chief industry of his beloved Lancashire, benefiting alike the cotton trade and all who depend on it for their living and prosperity. That, by his genius in planning and guiding research, he provided a sure foundation for ultimate success is evident from the review of the work of the Association to the end of 1926, recently published by the Shirley Institute under the title "Research in the Cotton Industry." Not improbably his work at Didsbury may come to be regarded as his best.

Crossley served the Chemical Society in many ways. He was an abstractor during the three years 1897–99 and a member of the Publication Committee for a period of twenty years ending in March 1926. From 1906, when he became Honorary Secretary, he held office without a break until his death, becoming Honorary Foreign Secretary in 1913, President in 1925 and on his resignation of the Chair, Vice-President in 1926.

The Annual General Meeting in 1926 was notable as being the first to be held out of London. Early in Crossley's presidency, the Council decided to make the experiment of holding the ensuing annual meeting in a provincial city. Most appropriately, Manchester was the city chosen, and the University the place of meeting. Crossley thus had the gratifying experience of occupying the Chair as President of the Society in the Chemistry lecture theatre in which he had sat as student under Roscoe and afterwards under Dixon, the latter of whom was present and took part in the proceedings. The presidential address was entitled "The Co-operation of Science and Industry," a subject constantly in his thoughts, to which he had also referred in a lecture on "Science and Industrial Problems" at the Royal Institution on February 5th 1915.

By nature Crossley was deliberate, but with his mind once made up resolute. Unfailingly courteous and genial to all in every relation of life, it is probable that comparatively few were admitted to the intimacy of his friendship. His recreations were typical: he played lawn tennis in his student days and golf later in life, but in billiards and fly-fishing—the latter absorbing entire holidays before the War—he found an abiding source of pleasure. To his culti-

vated taste books, of which at one time he was an eager collector, music and the theatre, made a strong appeal. Without being robust he enjoyed good health until the effect of the strain of the War years began to manifest itself. A voyage to Madeira in the May of 1925, after he had succeeded to the Presidency of the Society, gave a temporary respite, but in the autumn he was less well and early in January 1926 sought to resign office forthwith on medical advice. By relieving him of all work requiring his presence in London, the Council of the Chemical Society rendered it possible for the resignation to be deferred until the Annual General Meeting in March, thus enabling him to complete one year of office.

Before the summer was over, it was evident that his health was failing rapidly. Towards the end of the year he tendered his resignation of the Directorship of the British Cotton Industry Research Association, but by resolution of the Council remained nominally in office pending the appointment of a successor. This appointment had not been made and he was still Director when, on Saturday, March 5th, 1927, he died.

Crossley received many honours: D.Sc. (Victoria University) 1899; F.R.S. 1907; Hon. LL.D. (St. Andrews) 1917; C.M.G. 1917; Longstaff Medallist of the Chemical Society 1918; C.B.E. and Officier de la Légion d'Honneur 1919. In 1901 he married Muriel, daughter of Ralph Lamb of Liverpool, who with their son and daughter survived him. It may be permitted to add that the son, Kenneth Harwood Crossley, to the grief of all who watched his early career and had recognised his ability, tenacity of purpose and faculty for endearing himself to all with whom he worked, was drowned in a sailing accident off Llanddwyn Island, Anglesey, on July 30th, in his 23rd year. W. P. Wynne.

HILDYARD JOHN EGLINTON DOBSON.

Born February 18th, 1902; Died March 28th, 1927.

H. J. E. Dobson, in whom is lost a young physical chemist of high promise, was born on February 18th, 1902, at St. Michael's Vicarage, Southfields, London, where his father, the late Rev. R. A. Dobson, M.A., was vicar for 25 years. His family had a definitely scientific connection, for his uncle, Major George E. Dobson, of Netley, was a Fellow of the Royal Society and was a personal friend of Charles Darwin and of Huxley.

After nine years at school at Monkton Combe, near Bath, Dobson entered University College, London, in 1919, as a student of science. During his undergraduate course he showed great promise in

chemistry, sharing the Tufnell Prize, a coveted distinction in these laboratories. His honours degree, of an unexpectedly low class, was no index to his merit; and this he showed at once by the success with which, aided by the Department of Scientific and Industrial Research, he proceeded to tackle research at University College on problems of solubility and activity in aqueous solutions. Papers which were an outcome of this work were published in the *Journal* in 1924 and 1925; and these afford the first accurate data for the partial pressures of water in hydrochloric acid, and of both water and alcohol in aqueous alcohol. He made many invaluable improvements in the technique of vapour-pressure work, of which that recorded in the *Journal* (1924, **125**, 1968) is only one instance.

In October, 1924, he joined, by invitation, the staff of the then new chemistry school at Durham, as lecturer in physical chemistry. Here, in spite of an illness which postponed his beginning duty, he set about his new work with great zest and success. At the same time he carried on energetically his studies of solution, both theoretically and practically; his originality of thought began to develop very markedly; and he has left a considerable volume of data and calculations which, if his health had allowed him to carry them a stage further, would undoubtedly have afforded a valuable contribution to physical chemistry.

Dobson's indomitable gaiety, gentleness, and enthusiasm, which he kept even during the long illness which proved fatal, won him affection from all his associates, both in the laboratories and in the college (Hatfield) of which he was a member at Durham. I. M.

ALBIN HALLER.*

BORN 1849; DIED 1925.

ALBIN HALLER, the eldest of a family of eleven, was born on March 7th, 1849, at Felleringen, a village in the valley of Thann-Saint-Amarin and not far from Mulhouse. From the village school he passed to the higher primary school at Wesserling, and the spectacle presented by the large factories of this busy industrial centre undoubtedly stimulated his imagination. He wished to become an engineer, but, at the age of fourteen, was apprenticed as a carpenter in his father's workshop. Two years later, however, as the result of a conversation with a pharmacist of Wesserling, he was brought into contact with his " bon génie," M. Achille Gault, and this event altered the whole course of his life. Haller loved to

* Based on Madame Ramart's Notice in the *Bulletin de la Société chimique de France.*

recall the period between 1865 and 1870, from the day when he walked over the hill separating his native valley from Mulhouse in order to present himself at the house of his first teacher to the time of his gaining the baccalauréat ès sciences. M. Gault was quick to appreciate the character and rare ability of his pupil; during three years the leisure which the direction of a laboratory allowed was devoted to Haller's scientific education and he then became assistant to M. Gault's brother, M. Léon Gault of Colmar, who instructed him in French and Latin.

The Franco-Prussian war supervened and Haller volunteered at Belfort, but in the sorrowful year 1871 he lost his father and, choosing to remain in France, had perforce to leave his mother and all that he remembered on the other side of the frontier. At Nancy he rejoined M. Gault, who had come to found a pharmacy and now continued to assist Haller in preparing for pharmaceutical examinations. Soon the University of Strasbourg was installed at Nancy and Haller became in succession aide-préparateur (1872), préparateur, and chef de travaux at the École Supérieure de Pharmacie. In 1879 he submitted his thesis for the doctorat ès sciences and from this time his advancement was rapid, so that in 1885 he became a professor in the Faculty of Science of the University. In 1899 he was called to the University of Paris and proved to be a worthy successor of Friedel and of Wurtz, adding fresh lustre to an illustrious record by his numerous researches, by his inspiring teaching and especially by his ability to communicate something of his own enthusiasm to his students. Haller was an able and energetic organiser; in relatively early days he was the prime mover in the creation of the Institut Chimique in the University of Nancy (1890) and, later, of that devoted to the study of physical chemistry and electrochemistry (1897). He was throughout his career actively interested in the co-operation of science and industry, and not least among his many services to his country must be reckoned the important part which he played in developing the teaching of applied science in France. In 1908 he succeeded Berthelot as President of the Commission on Explosives, and both civil and academic honours were showered on the ardent patriot and distinguished savant.

The scientific work of Albin Haller, extending over a period of fifty years, presents a striking example of the achievement that is possible when penetrating vision, amounting to intuition, goes hand in hand with remarkable powers of observation and sustained effort. It is impossible to give in a short space an adequate idea of the ground covered by Haller's original memoirs (of which there are nearly 250), but his researches in the camphor and phthalein

groups and on the elegant syntheses with the aid of sodamide must be briefly described or rather indicated. Subjects which cannot even be touched upon are, for example, Haller's work on pseudo-acids, on alcoholysis and on optical rotatory power.

The study of camphor and its derivatives was the object of Haller's earliest researches and he never completely abandoned the subject, since even in 1925 certain of his collaborators were engaged in this fascinating field of enquiry. We owe to Haller the demonstration that camphor is a ketone of the formula $C_8H_{14}<\begin{matrix}CH_2\\CO\end{matrix}$ and he also effected the final stages in its synthesis. Haller treated sodiocamphor with cyanogen chloride and thus obtained cyanocamphor, $C_8H_{14}<\begin{matrix}CH\cdot CN\\CO\end{matrix}$; which could be hydrolysed with formation either of camphorcarboxylic acid or of homocamphoric acid, $C_8H_{14}(CH_2\cdot CO_2H)(CO_2H)$, according to the experimental conditions. The familiar syntheses of the latter acid and of camphor from camphoric acid through camphoric anhydride and campholide are due to Haller. If we are to appraise these contributions to camphor chemistry at their true value it is necessary to recall that it was Haller himself who demonstrated that camphoric acid is a dicarboxylic acid; Friedel had suggested that it might be a keto-hydroxycarboxylic acid and Ostwald, from a study of the electrical conductivity of solutions of the acid, was led to concur in this opinion. The preparation of arylidene and alkylidene camphors by the action of aldehydes or ketones on sodiocamphor was of importance not only because it proved that camphor contains the group $\cdot CO\cdot CH_2\cdot$ but also because these substances were found to possess interesting optical properties and could be used as the points of departure in further syntheses.

Haller devoted much attention to clearing up the relations existing between the isomeric borneols, both natural and synthetic, characterising the former by the preparation of the related camphor, bromocamphor and camphoric acid. He concluded that the borneols and *iso*borneols are stereoisomerides to be represented by one and the same structural formula.

In order to avoid the partial reduction that occurs when sodium is employed in the preparation of sodiocamphor, Haller in 1904 investigated the action of sodamide on camphor and found that the products of a smooth reaction were sodiocamphor and ammonia. Sodamide had previously been used in organic chemistry for different purposes by some chemists, for example, by Titherley, Freund, and Speyer and by Brühl, but in Haller's hands it became a powerful auxiliary and new general synthetic methods were based on its use.

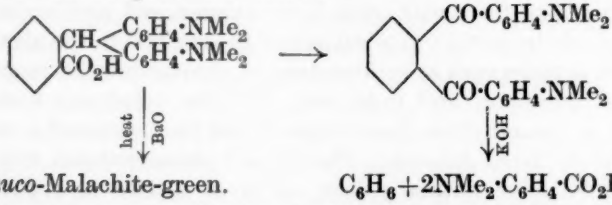
By its means the formation of the sodio-derivatives of ketones is a general reaction (acetone and acetophenone giving rise chiefly to condensation products) applicable to all substances of the forms $R{\cdot}CO{\cdot}CH_2R'$ and $R{\cdot}CO{\cdot}CHRR'$ and these sodio-derivatives may be brought into reaction with substances of various types. An important application is the progressive alkylation of ketones by means of sodamide and alkyl bromides or iodides through such stages as $R{\cdot}CH_2{\cdot}CO{\cdot}CH_2R$, $R{\cdot}CHR'{\cdot}CO{\cdot}CH_2R$, $CRR'_2{\cdot}CO{\cdot}CH_2R$, $CRR'_2{\cdot}CO{\cdot}CHRR'$, $CRR'_2{\cdot}CO{\cdot}CRR'_2$. The substances of the penta-alkylated acetone type are obtained by operating in ethereal solution and of them only pentamethylacetone reacts with hydroxylamine, semicarbazide and phenylhydrazine. The substances of the hexa-alkylated acetone type are obtained by operating in an aromatic hydrocarbon medium and do not condense with the above-mentioned reagents for the carbonyl group. On the other hand, these heavily substituted ketones may be readily and quantitatively reduced to secondary alcohols and, moreover, the ketones $Ph{\cdot}CO{\cdot}CR_3$, which are best prepared by Haller's method from the mono- or di-alkylated acetophenones, form with ease both oximes and semicarbazones. Haller made important applications of the method to the alkylation of cyclic ketones such as *cyclo*pentanone, *cyclo*hexanones, menthone, thujone, camphor, and indanone. He also employed such substances as trimethylene chlorobromide and thus obtained a series of δ-chloro-alkylated ketones. The polyalkylated ketones and their derivatives have naturally been of great service to students of molecular rearrangement and the theoretical interest of the study of their reactions and properties is inexhaustible.

Whilst carrying out experiments on the condensation of benzophenone and its derivatives with sodiocamphor (that is, camphor and sodamide) Haller noticed the formation of aromatic acids and amides. He was able to show that sodamide and benzophenone yield an additive product that is decomposed by water with the formation of benzamide, benzene, and sodium hydroxide. This decomposition was then found to be general for ketones of the form $R{\cdot}CO{\cdot}CR'R''R'''$, yielding either $R{\cdot}CO{\cdot}NH_2$ and $CHR'R''R'''$ or RH and $CR'R''R'''{\cdot}CO{\cdot}NH_2$ according to the nature of the substituents. A careful study was made of the circumstances governing the direction taken by the reaction and many interesting points emerged. Although there are exceptions, it was found to be a general rule that where the decomposition could yield an aromatic or an aliphatic acid amide, the latter course was favoured; *e.g.*, phenyl *tert.*-butyl ketone yielded benzene and pivalamide: $Ph{\cdot}CO{\cdot}CMe_3 + NH_3 \longrightarrow C_6H_6 + CMe_3{\cdot}CO{\cdot}NH_2$. Especially important in view of the use which Bouveault made of the method in con-

nexion with the chemistry of fenchone and camphorone is the extension of the study of this decomposition in the group of the cyclic ketones. Haller showed that fluorenone is changed by sodamide (and subsequent treatment with water) into *o*-phenylbenzamide. Similarly, 2 : 2′-dimethylindanone yields phenylpivalamide, which, like many of the products of these reactions, is difficult to obtain in other ways. As a third example, selected from many, the decomposition of dialkylated camphors by sodamide was found to yield the dialkylcampholamides.

Haller has also employed his method for the synthesis of certain pyrrolidines and tetrahydropyridine derivatives and in many other directions.

Whilst he was still at Nancy, Haller, in collaboration with Guyot, made some extremely interesting studies of certain phthalein, phthalophenone and anthracene derivatives. These were connected with the establishment of the constitutions of chemical individuals and with the mode of occurrence and mechanism of such transformations as those represented below.



leuco-Malachite-green. $C_6H_6+2NMe_2\cdot C_6H_4\cdot CO_2K$

Haller obtained the chloride of *o*-benzoylbenzoic acid in a crystalline condition and since it readily condensed with benzene in presence of aluminium chloride with formation of diphenylphthalide, he concluded that it should be formulated as phenylchlorophthalide. Another fruitful investigation was concerned with the preparation of *o*-(*p*-dialkylaminobenzoyl)benzoic acids and their conversion into the hitherto unknown dialkylaminoanthraquinones by successive reduction, cyclisation by condensation, and oxidation. Finally, by applying the Grignard reaction to anthraquinone, Haller made a long series of 9- and 10-arylated anthracenes and dihydroanthracenes.

The illness which proved so rapidly fatal was provoked by a laboratory accident and thus, at the age of seventy-six, Haller was carried away whilst still actively engaged in experimental work. He had expressed a wish that the end might come in this way.

Albin Haller was an inspiring and beloved teacher, a highly successful investigator of world-wide renown, and a great Frenchman, but he was also a man of fine character and as modest as he was distinguished.

R. Robinson.

RUDOLPH MESSEL.*

BORN JANUARY, 1848; DIED APRIL, 1920.

RUDOLPH MESSEL was the son of Simon Messel, a banker of Darmstadt. He was the second of five children, of whom four were to make their homes in England; the fifth acquired great distinction as an architect in Berlin. He lost his father when 11, and shortly after was sent to a Huguenot school at Friedrichsdorf in the Taunus, where he remained until he was 15 years old. His schoolmaster, Philip Reis, was the inventor of the first telephone. Messel, in his Presidential Address to the Society of Chemical Industry in New York in 1912, makes reference to the fact that he "assisted Reis in making the mechanical parts of some of his instruments and also repeatedly in his experiments, Reis being at one end of the circuit, speaking or singing, I listening at the other, or *vice versa*." About this time the family circumstances changed, and it was clear that Messel would have to become self-supporting at an early date. It was his intention to become an engineer, and in 1863 he discussed his further course of action with an old friend of his father's, H. Rau, then living in Frankfort. Rau appears to have advised Messel to devote himself to the study of commerce which he said would rapidly lead to independence, and to combine with this the study of Chemistry, Physics and Technology, and so become a manufacturer. It is clear that Messel's whole course of action was influenced by this letter, as not only did he keep it to the last among his rarest letters, but followed the advice it contained almost verbally.

In April, 1863, he became apprenticed to E. Lucius in his wholesale drug and chemical factory in Frankfort, and remained there until September, 1866, leaving to enter the Federal Polytechnic in Zurich, where he followed the regular first-year course. The following winter he spent at Heidelberg, studying physical chemistry under Erlenmeyer. He moved in the spring to Tübingen, where he finished his education, studying chemistry under Strecker, and continuing with him until April, 1870, carrying out work for which he obtained his degree. In April, 1870, he came to Manchester, originally to act as private assistant to Roscoe.

He was recalled to Germany owing to the outbreak of the Franco-Prussian war, where he served as a stretcher-bearer in the army of the Loire and was wounded. When recovered, he returned to England, where he remained during the rest of his life and ultimately became an Englishman.

He entered the service of Messrs. Dunn, Squire & Co., Stratford, as assistant to Dr. Squire. Shortly after, Squire formed with

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Spencer Chapman the firm of Squire, Chapman & Co., and took Messel with him in his new venture. This change occurred at a time when the growth of the synthetic dyestuff industry was threatened by the excessive price which was charged for fuming sulphuric acid, then produced by the old Nordhausen process in Bohemia. Squire decided to commence the manufacture of fuming acid.

In his New York Presidential Address, Messel tells of a conversation in the beginning of the '70's with his former teacher Strecker, and Brüning of Höchst, on the importance of fuming sulphuric acid in the synthetic alizarin industry. To his question how the acid should best be made, Strecker gave the reply: "That is a problem for you to solve." A few experiments convinced him, he says, that, given pure gases, the catalytic action of platinum was the rational solution of the problem. In April, 1875, a telegram came to him at the laboratory from Squire, asking him to read up that night about Nordhausen acid, as it was wanted by an Alizarin Works. The response was immediate and typical—no reading was necessary. Next day he showed how simple a matter it was to unite sulphur dioxide with oxygen by means of platinum. However, Squire was conventional and thought that the decomposition of acid sulphate would be a simpler method. Experiments were made, as requested, but eventually Messel was told to try his dodge.

Of the work that followed, no permanent record has been published, except in the form of Patents taken out by Squire in 1875. A year later, however, in April, 1876, Squire and Messel described and demonstrated the process before the Chemical Society. This paper was never printed, probably because of the Patent situation, but a paragraph in the "Chemical News" records the meeting. Messel treasured until his last days a document describing the experiments, and the original platinum apparatus used was left by him in his will to his lifelong friend, Professor H. E. Armstrong.

In his Presidential Address, Messel refers to the publication in October, 1875, by Winkler, of a process which was practically identical with his. Both investigators erred at that time in believing that stoichiometrical proportions of the gases were the best to use, and the various similarities gave rise to unpleasant comment. In letters to Messel, however, Winkler freely acknowledges the independence of Messel's work, and only regrets that he had deprived himself of the benefit of the invention by his publication.

The process was established at Silvertown, and in 1878 Messel succeeded Squire as manager of the works, which he only quitted in 1915, when his health gave way under the excessive strain of the times. The firm became Spencer, Chapman & Messel, Ltd., and the factory grew in size and importance.

Messel remained a bachelor and lived on the works. He was an indefatigable worker, and set a very high standard to all those who served under him. His sense of justice and sympathy, and the fact that he lived amongst them, gave him great popularity and power with his workpeople.

In the early days of the industry, the value of the fuming acid was much greater than that of oil of vitriol and the most suitable mixture of sulphur dioxide with oxygen was made by decomposing the latter. As experience was gained, and the difficulty of condensing the anhydride was overcome, sulphur dioxide prepared by burning sulphur and ordinary air were used, and later, excess of air was employed largely as a result of observation by the foreman that the plant worked better under these conditions.

It is a testimony to Messel's remarkable insight that right at the beginning he obtained such a wonderful knowledge of all details of this catalytic process, subsequently developed on a very large scale and in great detail by Dr. Knietsch and his co-workers of the Badische Anilin und Soda Fabrik.

Remarkable as Messel was as an industrialist, he was even more remarkable as a man. A man of astounding vigour and feeling, he had little thought for himself and a hatred of all display. He was essentially an artist, both in his extreme devotion to his own art of chemistry and in his love of the company of artists and other bohemians. He was everything—not only chemist, engineer and business man, but also took care to cultivate the social side of his life, and was almost the only manufacturer of his day who attended regularly at scientific gatherings and showed a real interest in the proceedings. His vigorous frame, black hair and sparkling eyes, his smiling face and peculiar guttural accent will remain in the memory of all who knew him. He never mastered English properly though he spoke it fluently. He was very fond of young people, many of whom rejoiced in his generosity. One of the most lovable of men, his outlook on life was always cheerful and optimistic. The example he set in leaving his fortune to science is a remarkable one and best proof of his considerate outlook. Honest and sincere himself, he hated insincerity and all meanness of spirit.

He played an active part in many scientific societies, particularly the Society of Chemical Industry, of which he was Foreign Secretary for many years and President for 1911–1912—probably the only connection in which he showed vanity, but he was very proud also of his election to the Royal Society in 1912.

His Presidential Address was written to show that science and industry are working hand in hand, and the importance of the results that such co-operation has produced. In discussing the

education of a chemist, he stressed the fact that too early concentration on special subjects had a bad effect on the development of the power and habit of thinking independently and on the faculty of imagination in the student. He held that technique is very rapidly acquired in practice by one who has been scientifically trained. With Carlyle he said, "He who has learned how to learn can learn anything," and the best system of education is the system which teaches each man how to educate himself. Gifted with his full share of enjoyment of the good things of this life, Messel nevertheless led a life of great simplicity. His success was due, in the first place, to his thorough scientific training and scientific outlook, but in an exceptional degree to his moral attitude towards his work.

He left four-fifths of his residuary estate to the [Royal] Society and the remainder to the Society of Chemical Industry. Without imposing any trust or obligation, he desired that the capital should be kept intact and the income applied to the furtherance of scientific research and other scientific objects. E. F. A.

IRA REMSEN.*

Two men, Ira Remsen and Wilhelm Ostwald, stand out during the last fifty years as great teachers and as founders of chemical journals which have had a profound influence on the development of chemistry. In these two respects their work is comparable with that of Liebig during the middle of the nineteenth century.

Ira Remsen was born in New York City, February 10th, 1846. His parents were both descended from the early Dutch settlers of New York and his mother had also Huguenot blood in her veins. For two years, from eight to ten, the boy lived in the country and had that intimate contact with nature which is impossible for a lad who spends his life exclusively in a city. A part of his early education was received in country schools. After further study in the public schools of New York City he entered the Free Academy, now the College of the City of New York, where he studied Latin, Greek, mathematics, history and a very little science. He did well in Latin and Greek and it was doubtless during those years that he laid the foundation for that perfect command of accurate English which has made it such a delight to read his books and to listen to his lectures. His interest in science seems to have been awakened at this period by the popular, illustrated lectures given by Dr. Doremus at the Cooper Institute.

He did not, however, complete the four years of work required

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for graduation at the Free Academy. Many years later he received the bachelor's degree from the College of the City of New York, as of the class of 1865. He was accustomed to say, with some pride, that he was one of the few men who had received the rank of M.D. from the College of Physicians and Surgeons without having received the bachelor's degree. He also said, at one time, that he thought he was the only university president in America who had not completed a four years' college course

After a few years in the Free Academy, Remsen's father decided that he should become a physician and apprenticed him to a doctor who taught in a homœopathic medical college. Here he read some chemistry and tried some chemical experiments for himself, sometimes with disastrous results to his fingers and clothing, as he told his students in recalling those days. He attracted the attention of his preceptor, however, and was made lecture assistant and quiz instructor in the college.

He soon revolted at the inefficient instruction and induced his father to send him to the College of Physicians and Surgeons of Columbia University. At the age of twenty-one he graduated and was supposed to be ready for the practice of medicine.

Once more he refused to be guided by the wishes of his father and, instead of entering a desirable partnership, which was offered him, with a well-known physician, he set out for Germany to study chemistry.

Liebig's name had attracted him to Munich and he had not learned that the great master had given up the direction of students some time before and had gone to the Bavarian University with the understanding that he could devote his time to his own studies and writing and that his duties should consist in giving a single course of lectures in inorganic chemistry. Remsen was forced to study with an able *Privatdocent*, Jacob Volhard. From him he received his first systematic laboratory instruction. Before that he had never performed the simplest analysis. Thorough training in analytical chemistry was, at that time, considered to be the only routine laboratory work necessary for the preparation of a chemist to begin research, and we may be sure that the fundamental basis for his career was well laid during this year of intimate association with Volhard.

During the summer of 1868, Wöhler made one of his friendly visits to Liebig and, through Volhard, Remsen was introduced to him and arranged to go to Göttingen in the fall. There he began research work under the direction of Fittig and two years later received his degree of Ph.D. at the age of twenty-four. When we remember that Remsen spent only one year in the systematic study

of chemistry and two years in research in earning his degree, we are tempted to question whether the long years of routine instruction which are required of young chemists to-day do not tend to dim that eager enthusiasm and repress the initiative so invaluable for a successful career.

It does not follow, however, that because Remsen did not take the varied courses of routine lectures which we expect of students to-day he failed to become very thoroughly acquainted with the chemistry of his times. He once told me that during his stay in Germany he read the volumes of Liebig's *Annalen*—150 volumes had been published in 1870—until he was acquainted with all the important papers published in that journal.

The same year that Remsen received his doctor's degree, Fittig was called to the professorship at Tübingen and he asked Remsen to go with him as his lecture and laboratory assistant. He continued in this position for two years and in this way, for five years in all, he drank in the spirit of the German laboratories.

It was a fortunate time for the eager, enthusiastic young man. In 1858 Cannizzaro had shown the importance of Avogadro's principle and laid the foundation for a system of true atomic weights. The same year, Couper and Kekulé extended Frankland's doctrine of valence to explain the structure of carbon compounds, and hundreds of professors and students were working together, after the model of Liebig's laboratory, in the fascinating world of organic chemistry.

It was at Tübingen, too, that a young Scotchman rang at the door one day and asked, in broken German, for the "Vorlesungszimmer." Remsen answered, "Oh! I guess you want the lecture room." So there was begun the life-long friendship with Sir William Ramsay. Only a few months before his death, Sir William wrote to Remsen, "Well, I am tired and must stop. I look back to my long friendship with you as a very happy episode in a very happy life; for my life has been a very happy one." When Remsen helped with the plans of the Kent Chemical Laboratory of the University of Chicago, he provided few rooms for isolated students and he made the remark that students learn more from each other than from their teachers. When two such students as Ramsay and Remsen met, we can well believe that this was true.

Remsen returned to America in 1872 and, after some delay, was appointed professor of chemistry and physics at Williams College. When he assumed his duties he found no laboratory and scant encouragement to teach science other than as a small element of general "culture" in an old-fashioned classical college. After a year, he was furnished a laboratory for his own use and there he

carried on researches on the action of ozone on carbon monoxide—a subject to which he returned some years later—and on *p*-sulphobenzoic acid. The latter led to an attempt to oxidise *o*-sulphobenzoic acid and its sulphamide and this, in turn, led to a long series of investigations carried out with students at the Johns Hopkins University. These studies finally established "Remsen's Law" that groups in the ortho-position interfere with the oxidation of alkyl groups of aromatic compounds by means of chromic or nitric acid.

As an illustration of the spirit of the New England colleges of that day, the following incident related by Professor J. M. Kingsley is illuminating:

"In the autumn of 1874, together with the rest of the junior class in Williams College, I began the study of chemistry under Professor Ira Remsen. After a few days I asked him for the privilege of carrying my studies farther in his private laboratory, as there was no laboratory work connected with the regular course. He replied to the effect that he would have to lay my request before the faculty, as there was no provision for such work in the curriculum. A few days later he asked me to stop after the class was dismissed, and then he informed me, in the most disgusted tones, that 'The Faculty, *in their wisdom*, have decided that you would break too much glassware and waste too many chemicals to allow you to work in my laboratory.'"

Kingsley became a zoologist of note instead of a chemist.

Shortly after his return to America, Remsen published a translation of Wöhler's "Organic Chemistry." He also published a beautifully written "Theoretical Chemistry." These books, and still more his persistence in research under discouraging conditions, attracted the attention of President Gilman, who was seeking men for his faculty at the Johns Hopkins University. He had already secured Gildersleeve for Greek, Rowland for physics and Sylvester for mathematics. Remsen was invited to Baltimore to meet the Board of Trustees and was entertained at a dinner at which he was seated beside one member of the board after another. In this way Professor Remsen became one of that galaxy who worked with President Gilman to organise the first genuine university in America, where more than half the students were graduates of other colleges and where the purpose was not so much to teach what is already known as to develop men into productive scholars and add to the world's knowledge. President Gilman had the somewhat rare quality of fully trusting the men he selected and allowing them to develop the work of their departments without interference. His injunction to Remsen was, "Do your best work in your own way."

Professor Remsen followed rather closely the models with which

he had become so familiar in Germany. He gave lectures on inorganic chemistry during the first semester and on organic chemistry, the second. These were well illustrated with experiments and he had a crystal-clear, masterful method of presenting his subject. Once a week there was a meeting of graduate students for reports on current literature.

But the most important and vital part of his instruction was the daily visit to the desk of each research student. Often, at critical points, he would stop and work for minutes or for an hour or more with the student, and the product, in the end, was the joint work of professor and student, as it had been in Liebig's laboratory. Most of the topics studied grew, directly or indirectly, from his investigation of the oxidation of *p*- and *o*-sulphobenzoic acids and the law of the protection of ortho-alkyl groups from oxidation.

Quite early in the course of these studies, Fahlberg, working under his direction, discovered that the *o*-sulphamide of benzoic acid may be easily oxidised by potassium permanganate in a neutral or faintly alkaline solution. The product was called by Remsen benzoicsulphinide. It is several hundred times as sweet as sugar and some years later Fahlberg developed the commercial production of the compound under the name of saccharin.

The discovery of benzoicsulphinide naturally led to the investigation of many other similar compounds. This also led, rather directly, to the discovery of the sulphonephthaleins and the study of the chlorides of sulphobenzoic acid. Professor Reid reports how he came to study the decomposition of diazonium compounds with alcohol. The laboratory book said "add alcohol and smell the aldehyde." A student came to him and said he did not smell aldehyde. Remsen took the tube and could not smell aldehyde either. He made this into a good story, telling how stubborn the student was who wouldn't smell aldehyde when told to do so.

The work of Professor Remsen and his students never degenerated into the mere preparation of new compounds. He always endeavoured to establish some general principle in relation to the substances prepared.

In 1883 Professor Remsen came back to the action of ozone on carbon monoxide and a very careful investigation demonstrated that the latter is not oxidised when the mixture with ozone is heated to 300° and the ozone is completely decomposed. He also, in an investigation which proved that phosphorus usually contains a little carbon, demonstrated that carbon monoxide is not oxidised when mixed with air and passed over moist phosphorus, although ozone is formed in quantities. A satisfactory theoretical explanation of these remarkable results is still to be found.

In 1889 Professor Remsen made an exhaustive study of the literature of the double halides and found that, with very few exceptions, the number of molecules of an alkali halide combined with one molecule of another halide is equal to or less than the number of atoms of chlorine in the other halide. A considerable number of experimental investigations were carried out with his students to test the validity of this generalisation. The conclusion that two chlorine atoms unite to form a bivalent group has not been generally accepted and does not agree well with the more recent electronic theories of chemical combination.

When Remsen went to Johns Hopkins University in 1876, there was no satisfactory medium in America for the publication of an account of his researches. A few of his articles were published in *The American Journal of Science*, but Professor Dana, the editor of that journal, soon decided that researches in organic chemistry did not furnish material of sufficient interest to his readers and advised publication abroad. Professor Remsen was not satisfied with this and, with the aid of other chemists, he established *The American Chemical Journal*. With far-sighted vision, he made this a medium of publication for American chemists and not an organ of the Johns Hopkins University. For thirty-five years this journal was a very important agency for the promotion of genuine chemical work. It was the first American journal in this field which secured widespread recognition abroad and it would be difficult to overestimate its value in stimulating chemical work and in placing Americans in their rightful place among the chemists of the world. At the close of the fiftieth volume President Remsen decided that publication in America would be better served by incorporation of *The American Chemical Journal* with *The Journal of the American Chemical Society*. This was done and the latter journal carries on its title page a record of the consolidation of the two journals.

Remsen's first book was a "Theoretical Chemistry," written while he was at Williams College. It passed through five editions and was translated into German and Russian. His "Organic Chemistry" was published in 1883 and has been the medium through which many chemists, physicians and others have been introduced to the subject. His text-books of "Inorganic Chemistry," both elementary and advanced, are characterised by a logical, lucid style which has made them very popular and widely used. The "Organic Chemistry" was translated into many foreign languages and several of the other books were also translated.

A long series of students, trained in intimate association with Professor Remsen, are now widely scattered and many of them hold important positions as teachers and in the industries. They

look back to him as to a father, who always required high quality in their work, who was wise in his advice and helpful in their difficulties.

Professor E. E. Reid writes, "It is impossible to characterise or describe Remsen. He had a keen sense of humour and a ready wit, a personality in the fullest sense of that term. He drew people to him but always kept them in their place."

In 1881 Boston had trouble with her water supply and Professor Remsen was called upon for his advice. He was fortunate enough to discover the cause of the difficulty. On many other occasions he was called upon for public services to Baltimore, Maryland, and the United States. He was for some years a member of the Good Roads Commission of the state.

In 1901 Remsen succeeded D. C. Gilman as president of Johns Hopkins University. The resources of the university had been depleted by the depreciation of some of its securities and the period of his administration was a difficult one. In spite of this, the university continued its steady and satisfactory development. The school of engineering was founded and the cramped quarters in the heart of the city were exchanged for the magnificent campus which the university now occupies in the outskirts of Baltimore.

President Remsen retired in 1913. After that he spent his time in travel, in revising his books, in work for the Government as chairman of the Referee Board organised during Roosevelt's administration to consider questions pertaining to the law for the control of food products and their adulteration, and in consulting work for one of our largest industrial corporations. He died at Carmel, California, in 1927, at the age of eighty-one.

He was the recipient of many honours. The degree of LL.D. was conferred by Columbia, Princeton, Yale, Toronto, Harvard and Pennsylvania. He was a foreign fellow of the London Chemical Society and foreign member of the French Chemical Society. In 1902 he was president of the American Chemical Society; in 1903, of the American Association for the Advancement of Science. During 1907—13 he was president of the National Academy of Sciences. In 1908 he was awarded the gold medal of the Society for Chemical Industry and in 1910 was president of that society. In 1914 he received the Willard Gibbs medal of the Chicago Section of the American Chemical Society.

In his boyhood Remsen was reared in a very strict, religious atmosphere and he retained a simple religious faith throughout his life. In his address "On the Life History of a Doctrine," delivered as president of the American Chemical Society, after pointing out that "faith is called for at every turn in scientific matters as well as spiritual," he said, "It would be as illogical to give them (atoms)

up as it is, in my opinion, to deny the existence of a power in the universe infinitely greater than any of the manifestations familiar to us; infinitely greater than man; a power that 'passeth all understanding.'"

WILLIAM A. NOYES.

EDWARD HENRY RENNIE.

BORN 1853; DIED JANUARY, 1927.

THE intellectual life of Australia suffered a heavy loss early last January, when Dr. Edward H. Rennie, Angus Professor of Chemistry in the University of Adelaide since 1885, died suddenly from heart failure at the age of seventy-four. Though he had long earned retirement, he remained in active work to the last, devoted, as always, to the promotion of education and of science in Australia.

His affection for that sunny land was native—not acquired, as it has been by so many of those engaged in University work there; for he was born and educated in Sydney, where his father, E. A. Rennie, was Auditor-General of New South Wales. His urge towards an academic life is, no doubt, to be traced back to his grandfather, James Rennie, who was Professor of Zoology at King's College, London, nearly a century ago. After graduating in Arts at the University of Sydney, he spent a few years as a school teacher there and in Brisbane; but in 1877 he went to London, bent on pursuing the study of chemistry. Before returning to Australia in 1882, he had obtained the London D.Sc. and had published a number of papers in the *Journal* of the Chemical Society. Some of these were on work done conjointly with Alder Wright, whose assistant he was for a time at St. Mary's Hospital Medical School. He came also under the influence of Professor H. E. Armstrong (the stimulating effect of which so many young chemists then and later could testify to), and the friendship thus formed lasted through his life, maintained by correspondence and revivified in 1914, when the British Association visited Australia.

Apart from certain investigations with Alder Wright in chemical dynamics (a subject then in a somewhat embryonic state), Rennie's researches at this time were organic and for the most part dealt with the chemistry of various Australian plants. His special interest in this field was to remain with him always. During the first ten years of his tenure of the Adelaide chair he contributed to the Society's *Transactions* seven papers on various Australian plant products; but thereafter he had but little leisure from teaching and administrative duties, and some of it was given to inorganic and

physical work. More recently, however, he took up the investigation of the resins of *Xanthorrhœa*, a peculiar and characteristic Australian plant.

As a teacher, Rennie was exceptionally conscientious and thorough. He had but little assistance, for it is only of late that the Australian Universities have been able to indulge in elaboration of staff (still very incomplete), and he found it necessary personally to teach chemistry in all its branches, organic, inorganic, physical, and analytical. The writer, who saw as much of him as was compatible with residence five hundred miles apart, can testify to his zeal in keeping abreast of modern advances, even in fields that did not specially appeal to him.

As a member of his faculty and of the governing council, frequently as acting Vice-Chancellor, and as chairman of the affiliated School of Mines, he did invaluable work for his University. In wider fields too his wise judgment, experience, and authority were of service to the country. He was the chairman of the South Australian branch of the Commonwealth Council of Science and Industry. In the last year of his life—perhaps the busiest—he was President of the Australian Chemical Institute and also President of the Australasian Association for the Advancement of Science; and his address at the Perth meeting of the Association included a valuable survey of Australian plant chemistry, past, present, and future.

As a man, Rennie was of simple tastes and rather austere habit of life, and there was an orthodox side to him best known to his fellow elders of the Chalmers Church in Adelaide. But his warmth of heart and human sympathy endeared him also to others. And the writer is among these; for Rennie, then a stranger, was the first to welcome him on Australian soil in 1886, and forty years of friendship followed.

D. O. M.

SIR WILLIAM AUGUSTUS TILDEN.

BORN AUGUST 15TH, 1842: DIED DECEMBER 11TH, 1926.

HASTED'S History of Kent states that John Tilden purchased Ifield Court, Northfleet, in 1766; the grandson of John Tilden was Augustus and had two sons, the elder being William Augustus, born in the parish of St. Pancras on August 15th, 1842. The brothers were unfortunate in their schooling. In 1845 their father had exchanged a clerkship in the Bank of England for the managership of the Kidderminster bank, but retiring from this post in 1852 he remained without business occupation until his death at Bedford

SIR WILLIAM AUGUSTUS TILDEN.

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in 1879; it thus happened that the boys were never kept for long at any one school. Their mother, however, was a woman of strong character and marked ability, devoting herself unreservedly to the care and instruction of her children during their early home-life; this benefit was uniformly recognised with affection by her sons, and having passed her concluding ten years in the household of William Augustus, she died in 1900 at the age of 94.

When eight years old the boy was placed as a boarder with Rev. Edward Brine, second master at Kidderminster Grammar School, remaining only two years because the family moved to Bedford. Here he was entered at the Commercial School, now called the Modern School, but after three years was transferred for one year to the charge of Mr. George Vasey, who limited his pupils to five, imposed upon them a vegetarian diet, and taught them the rudiments of anatomy, physiology, botany, zoology, mechanics and optics illustrated by diagrams which the lads were required to copy. Another break occurred in April, 1856. The boys' maternal grandfather, Mr. Henry Balls of Cambridge, had now undertaken responsibility for their education and he sent them to East Dereham, where Rev. Joseph Thompson kept a school of about 70; here William Augustus received his first contact with chemistry, and the demonstrations of a visiting master from Norwich inspired him with a desire to experiment on his own account.

Animated by the vague ambition to become a chemist, young Tilden was almost inevitably projected into pharmacy. His friends of that period would naturally reach a conclusion which remains, even after seventy years, a widespread popular superstition; and although the College of Chemistry was already operative under the direction of Hofmann, they cannot be blamed for what would then appear to be the normal procedure. So, in August, 1857, the lad was apprenticed for five years to a pharmacist of Barnsbury, Mr. Alfred Allchin.

This association was propitious, for Mr. Allchin took a liberal view of the relation between master and apprentice. He had been laboratory assistant at the Pharmaceutical Society, had worked for a short period in Paris with Pelouze and had joined the Chemical Society. Appreciating these advantages, he encouraged young Tilden to attend the Pharmaceutical Society's lectures on chemistry, pharmacy, botany and materia medica, permitting him to spend the whole of his fifth year in the laboratory of the School. Allchin's generosity was not limited to these benefits. He entered his apprentice for Hofmann's course of lectures at the Royal College of Chemistry, and this period was a critical one in the history of chemistry; for students were perplexed by the novel notation and

modified atomic weights introduced by Gerhardt and Cannizzaro. Hofmann's lectures were Tilden's compass, and in October, 1861, the young pharmacist gained the first Bell scholarship.

Another favourable influence on young Tilden was the friendship of Dr. John Stenhouse. Ill-health had led Stenhouse to relinquish his lecturership at St. Bartholomew's Hospital and equip a laboratory in Rodney Street, Pentonville, whence issued the series of investigations into natural products distinguishing the joint authorship of Stenhouse and Groves. Stenhouse frequently visited Allchin's pharmacy, greatly to the encouragement of young Tilden, whose preparative work he often commended, and whom he subsequently admitted to his laboratory as a junior assistant on sixty pounds a year. In 1863 Tilden became demonstrator at the Pharmaceutical Society under Attfield, who was then professor of practical chemistry while Redwood continued to give the lectures; and here he remained until 1872.

These nine laborious years encircled the transformation of a pharmacist into the chemist. In this development the London University system of graduation played an important part. Although no "cobbler from Cornwall," Tilden was one of an abundant upward-struggling community to whom the prospect of a definite academic hall-mark offers an elevating incentive to self-improvement. He toiled at French, German, Greek and Latin for matriculation, and in 1868 graduated B.Sc. with honours at an age which disqualified him from gaining the university scholarship. This was followed in 1871 by the D.Sc., in those days attainable by examination only; Tilden's examiners were Debus and Odling. Meanwhile, in the scanty leisure snatched from these pressing demands, he began publishing papers in the Journal of the Chemical Society, his first contribution (1865) dealing with periodides of organic bases.

A new chapter opened in 1872, when Tilden was appointed senior science-master at Clifton College, under the headship of Dr. John Percival, afterwards Bishop of Hereford. At that date the school was ten years old, and was directed by a remarkable man. Percival had proceeded from Rugby to Oxford (1854—58) and there took firsts in classics, mathematics, and physics; he aimed at moulding Clifton as an all-round school, a breakaway from the purely classical tradition, and his first group of assistants included A. Leipner, afterwards professor of botany at University College, Bristol. Later teachers of chemistry and physics were A. W. Reinold, John Perry, Tilden, and Shenstone, the first laboratories being opened in 1866 and followed by those for biology and zoology in 1869. The standard of effort appears to have been high. Laboratory classes, lecture courses and private coaching could not have left much time

for his own experiments, but somehow Tilden found it, and found also a valuable collaborator in W. A. Shenstone. The partnership was happy for both. Tilden had married before leaving London, and Shenstone was one of the household during the two years preceding his transference to Taunton in 1875. A joint paper on aqua regia and the nitrosyl chlorides appeared in that year, and work there described was the progenitor of pinene nitrosochloride. With exacting enthusiasm, for he was not physically strong, Shenstone went over to Clifton for the long vacation following his transfer, and the friends occupied their holiday in rectifying such essential oils as were then available, separating the terpenoid components and converting these into nitrosochlorides by the new agency. The results were published in 1877, and came to be recognised as a turning-point in the path of terpene chemists, leading to a fresh view of the hydrocarbons themselves and providing a trustworthy means of identification.

Meanwhile, an important municipal development had proceeded in Birmingham. Sir Josiah Mason (1795—1881), having amassed a fortune from humble beginnings, had the noble ambition to provide for others the educational opportunities denied to himself, and allocated £180,000 to the foundation of Mason College. The new institution was opened in 1880 and Tilden was appointed the first professor of chemistry in association with J. H. Poynting (physics), M. J. M. Hill (mathematics), and T. W. Bridge (biology). It may be readily imagined that the task of building up the organisation and tradition of Mason College would evoke physical and mental resources of a high order, and the success with which this early work was accomplished is reflected in the great midland university at Edgbaston representing the modern response of Birmingham to its largely augmented educational demands. The part which Tilden played in this constructive labour merits the fullest possible recognition. In addition to high professional competence early marked by election to the Royal Society (1880), he was endowed with a social quality which is unhappily rare. It has been said that the really well bred man is he who can enter —and leave—any mixed company of people to whom he is unknown without necessarily revealing his occupation in life. The searching requirements of such a specification were engagingly met by Tilden, whose conversation and appearance would have puzzled a casual acquaintance to decide whether he was an army officer, Indian civil servant, artist, metropolitan magistrate, man of leisure, or even an ambassador.

Adaptability so wide and graceful was particularly valuable in a society of the complexity comprised in Birmingham of the eighties. To harmonise aspirations of prosperous young amateurs with more

serious ambitions of the needier students; simultaneously to convince the Birmingham citizens that a man of science is not necessarily an eccentric anchorite, but that in belonging to their own world he might add to its attractions; withal to develop an ever-widening grasp of a rapidly growing science, were tasks which few chemists of his generation could have accomplished so successfully. At the beginning of his tenure, moreover, Tilden found that provision for instruction in metallurgy had not been made, and being without practical knowledge of the blast-furnace and steel manufacture, he became indebted to several of the large ironmasters, including Mr. Robert Heath, then M.P. for North Staffordshire, and Sir Isaac Lowthian Bell for the privilege of admission to their works. Soon afterwards, however, this branch of the curriculum was entrusted to Mr. Thomas Turner, who subsequently became the professor of metallurgy. In spite of these demands, Tilden continued the research on terpenes which had begun so auspiciously at Clifton. The first completed work dealt with decomposition of the hydrocarbon vapours by heat, and it was during a study of isoprene produced in this manner that its transformation into caoutchouc was discovered. Thus, both scientifically and socially, Tilden's life in Birmingham was a full and active one. He occupied a pleasant house in Harborne Road, took interest in his garden and continued to enjoy lawn-tennis until well past his fiftieth year. This may not appear unusual to a generation witnessing that indefinite extension of youthful activities engendered by golf, automobiles and jazz-discords; but post-war youth, rivalled in its thirst for amusement by a crowd of age-defying seniors, cannot be expected to realise that in those days men were "too old at forty," while coeval women wore caps.

Tilden's life was now widening its boundaries, for his reassociation with London grew considerably during the last few years of his Birmingham connection. He had executed several examinerships, including that in chemistry for the Science and Art Department; he sat in the council of the Royal Society (1892—4), and a continuous adherence to the Institute of Chemistry had culminated in his election to the presidency (1891—4). This office in particular made heavy calls on Tilden's time and attention, for the period was a critical one in the history of the Institute. Much controversy centred in the question of admission and the type of training which might most appropriately lead thereto. Several conferences took place; regulations were finally accepted in October, 1893, and remained the basis of those controlling admission during the twenty years following. The two main requirements were (1) three years of systematic training in chemistry, physics, elementary mathematics

and an optional other branch of science, associated with (2) three examinations, preliminary, intermediate (in general theoretical and practical inorganic and organic chemistry), leading to the final, in a branch of chemistry elected by the candidate from a prescribed list. Concurrently with this consolidation, an important geographical change occurred. Since 1884, the Institute had been a tenant of the Royal Statistical Society at 9, Adelphi Terrace, depending on the hospitality of the various London laboratories for examination facilities. At the beginning of 1893, however, the Institute moved to 30, Bloomsbury Square, thus for the first time enjoying dignified and ample premises of its own. Having acquired the remaining twenty-two years of lease, it seemed justifiable to build and equip the laboratories necessary for conducting practical examinations, and they were formally opened by the president on December 8th, 1893. In the same year the bye-laws were revised, and authority was given to an important definition by the censors concerning professional conduct; a seal was designed, incorporating the figure of Priestley as represented in Williamson's statue viewed from the old Mason College windows.

In the autumn of 1894, Tilden succeeded T. E. Thorpe as professor of chemistry in the Royal College of Science, London, and was destined to remain at South Kensington until 1909, when Sir Edward Thorpe returned for three years on retirement from the Government Laboratory. The period of Tilden's occupancy was important in the college history, covering the transference of the chemistry department from the conspicuous red building on the eastern side of Exhibition Road to its present domicile. Moreover, the change was concurrent with a modification in status effected by incorporating the Royal College of Science and the Royal School of Mines with the Central Technical College of the City and Guilds of London Institute: this occurred in 1907, when the two royal colleges were detached from the Education Department and united with the Guilds' Engineering College to form the Imperial College of Science and Technology. In prospect and achievement this transformation threw much extra work on Tilden and his physics colleague, A. W. Rücker, the consequent interruption to their systematic duties beginning about 1899, when Sir Aston Webb was commissioned to prepare the plans.

These last fifteen years of Tilden's professorial career were crowded ones. Interwoven with his college duties were the periodical demands of the Board of Education examinations and the continuous attention he gave to the Chemical Society. The Royal Society, which he served as a Vice-President during 1904—6 was another time-absorbing interest, and for a brief term he joined the Senate of

London University, having been elected a Fellow in 1899. Although these various legitimate distractions inevitably diminished the time given to research, he nevertheless maintained an interest in the field which had brought him fame, and broke new ground by a systematic study of specific heat; this work was continued for several years, and the earlier results were assembled in the Bakerian Lecture to the Royal Society for 1900. It was not surprising that about the time he was due by age to retire, Tilden incurred a slight breakdown in health; his friends had sometimes wondered at the unfailing regularity with which he had fulfilled his duties, because he did not give an impression of robust physical condition at any period of his later life. In view of the difficulty found in replacing him, however, Tilden was persuaded to remain until a suitable successor (Sir Edward Thorpe) could be found, and this arrangement was facilitated by delegating the lectures to his trusted colleague, Dr. G. T. Morgan.

Liberation from official duties in 1909 was accompanied by the distinction of knighthood and the title of Emeritus Professor, but only changed the form of Tilden's mental activity. He had intended to continue the experimental work which had been so much interrupted in later years, and for this purpose retained the use of a laboratory at the Imperial College; but his physical condition precluded sustained bench-work, and the project was necessarily abandoned. His retirement to the home he had already made at Northwood was therefore devoted to literary pursuits which took shape in four books, "The Elements" (1910), "Chemical Discovery and Invention in the Twentieth Century" (1917), "Life of Sir William Ramsay" (1918), and "Famous Chemists" (1921).

These volumes represent a substantial achievement indeed for the eighth decade of any man's life, and bear testimony to the unabated ardour with which he assembled and imparted knowledge. They involved frequent and sustained consultations in the Burlington House libraries, and scarcely diminished the regularity of his attendance at scientific meetings. In fact, it may be stated here that among the many claims of Sir William Tilden's life to the respect and admiration of younger chemists was the devotion he showed to the Chemical Society by his constant attendance at its meetings. He became a Fellow on June 1st, 1865, joining the Council as an ordinary member thirteen years later. Thereafter, in one capacity or another, he served as councillor thirty-seven years, comprising twenty-eight as Vice-President and four as Treasurer (1899—1903), occupying the presidential chair in the period 1903—5; his last appearance in Burlington House—and he seemed to know it would be the last—was on March 27th, 1924, when he

spoke to a resolution at the annual general meeting. Thus, in various ways and always disinterestedly, he well and truly served the body which assembled most intimately his professional friends and their joint scientific interests. The Annual Reports on the Progress of Chemistry, inaugurated in 1905, will remain a lasting memorial to this loyal devotion, being the concrete feature of his presidency.

Before the foundation of the Imperial College, Tilden was appointed Dean of the Royal College of Science and the Royal School of Mines. He was awarded the Davy Medal (1908), received honorary degrees from the Victoria University, from Dublin and from Birmingham, and was elected a member of the Athenæum under Rule II (1907). In 1869 he married Miss Charlotte Pither Bush of St. Heliers, Jersey, who died in 1905 leaving one son, Mr. Philip Armstrong Tilden, the architect. His second marriage took place in 1907, Lady Tilden having been Miss Julia Mary Ramié, also of St. Heliers, and in the knowledge that his twilight years were happy, peaceful and well-ordered his friends too have been happy. His death occurred on December 11th, 1926.

Tilden's active participation in chemical research continued throughout a period of more than forty years, during the earlier part of which, as might have been expected from the contemporary chemical atmosphere and his association with pharmacy, his experiments dealt with natural products. Thus his first paper (1865) described periodides of caffeine, strychnine and brucine, and his next inquiry (1872) related to the crystalline substances obtainable from aloes, to which he returned several times (1875 and 1877); comparison was made between Barbadoes, Natal, Socotrine, and Zanzibar aloes, from which a derivative of methylanthracene, oxygenated to the composition $C_{15}H_{10}O_6$, was obtained with chromic acid. An early paper displaying keen chemical insight and skilful technique was that on aqua regia and nitrosyl chloride (1874), showing how the latter substance may be obtained as an individual and proving the composition of its molecule to be NOCl; at the same time, it was established that the supposed nitrosyl dichloride and dinitrosyl sulphate of Gay-Lussac were actually fortuitous mixtures.

It was a natural consequence that the new agent should be applied to organic substances, and a beginning was made with phenol (1874) which gave chloranil, followed by turpentine (1875) giving the subsequently famous nitrosochloride of pinene, from which " nitroso-terpene " was prepared by the action of alcoholic sodium hydroxide. It was at this period that Shenstone had joined Tilden, and the two young men were quick in recognising that the confusion prevailing in essential oil chemistry might be dispersed by the new weapon;

but it is evident from the title of their paper, "Isomeric Nitrosoterpenes" (1877) and the procedure therein described, that at this stage of the inquiry they expected the nitrosochlorides to be less important means of identification than the nitroso-derivatives obtainable from them by removing the elements of hydrogen chloride. Thus the nitroso-derivative made from turpentine (American and French), oil of sage and oil of juniper was found to be identical in each case, and was distinct from that formed when the nitrosochloride of hesperidine, caraway, and bergamot oils is heated. The authors, however, already believed that "the result of the further application of this method will be to show that a great many of the natural terpenes are merely physical isomerides not differing from one another in chemical constitution."

During the two following years (1878—9) the terpene-alcohol terpineol was characterised. Earlier workers (Wiggers, List, and Oppenheim) had found that dilute acids convert the crystalline terpene hydrate into an oil which they called terpinol and believed to have the composition $C_{20}H_{34}O$. Tilden's investigation showed the oily product to consist principally of terpineol, $C_{10}H_{17}\cdot OH$, associated with a hydrocarbon, $C_{10}H_{16}$, afterwards identified with dipentene. At the same period he studied the hydrocarbons of Russian turpentine oil, and published the views he had been led to form regarding the constitution of camphor and the terpenes.

After an interval of about five years there appeared his well-known paper "On the Decomposition of Terpenes by Heat" (1884). The process therein described is a fore-runner of the modern operation of "cracking" petroleum, and allowing for difference in the starting-materials, the products of the two changes correspond. It was found that when the vapour of turpentine oil is passed through a heated iron tube on which redness is just visible in darkness, gaseous and condensable hydrocarbons are produced in great variety. Dipentene, *p*-cymene and colophene, with smaller proportions of benzene, toluene and *m*-xylene were isolated, but the most important and interesting product was the volatile hydrocarbon, isoprene, C_5H_8, obtainable also by the dry distillation of caoutchouc. In this connexion it may be claimed that the earliest production of synthetic rubber was in the hands of Tilden (1892), because a few years after the foregoing investigation he noticed that in a closely sealed bottle containing a specimen of purified isoprene there had appeared a sticky product which, when withdrawn and manipulated, showed those properties of rubber subsequently associated with sodium-polymerised isoprene. Although aware of what had occurred, and displaying this rubber as an object of interest to his friends, Tilden did not standardise the conditions of transformation, and it is not

difficult to reconstruct his probable attitude of mind by remembering that automobiles were not even threatening to arrive, and that the "synthesis" was virtually a passage from one tree-juice to another by de-polymerisation *cum* re-polymerisation. Moreover, in spite of all the attention directed to this matter in the pregnant thirty-five years intervening, the exact conditions of transformation remain obscure.

Tilden reviewed at some length the confused ideas then (1888) current on the constitution of terpenes and later (1893) showed that dipentene does not give toluic acid on oxidation; he proved that the hydrocarbon recovered from dipentene dihydrochloride must be a mixture, because it yields over 27 per cent. of toluic acid. In the next few years (1893—1895) he resumed attention to nitrosyl chloride, preparing phenylazoimide by its action on phenylhydrazine in acetic acid and incidentally discovering an alternative method of preparing hydrazoic acid by hydrolysing *p*-nitrophenylazoimide. These experiments embraced a very wide range of typical unsaturated compounds in a study of nitrosyl chloride with reference to its additive capacity. Its action on amides was then surveyed, and while oxamide, oxanilide, succinimide, and phthalimide were indifferent, other amides were found to undergo loss of nitrogen and, in the case of asparagine and aspartic acid, chlorination; lævo-rotatory asparagine gave lævo-rotatory chlorosuccinic accompanied by fumaric acid.

About 1890, Tilden had received from the West Indies a butterlike solid occurring as a by-product in the manufacture of Montserrat lime-juice. Isolation and characterisation of limettin, so named from *Citrus limetta*, gave much trouble, and the investigation remained unfinished in Birmingham; but later (1902) he was able to show that limettin is 4 : 6-dimethoxycoumarin, $C_{11}H_{10}O_4$, giving phloroglucinol with concentrated potash, and undergoing chlorination, bromination, and nitration.

The concluding papers dealt with carbon compounds all related to the nitrosochlorides of pinene and limonene, thus providing a seemly epitaph to Tilden's early chemical interest. By the simple device of using an inactive mixture of American and French turpentine in place of an optical individual, the yield of nitrosochloride was greatly improved (1904), and was brought to the 55 per cent. obtainable from the inactive pinene produced when methylaniline or dimethylaniline acts on the nitrosochloride. This, and the two nitrosochlorides of limonene, were then found to exchange their chlorine atom for the cyano-group when heated with alcoholic potassium cyanide (1904—5), the products being unimolecular: the compound thus obtainable from limonene β-nitrosochloride was

identified with cyanodihydrocarvoxime. The corresponding pinene derivative is also a cyano-oxime, and undergoes hydrolysis in successive stages to an aminodicarboxylic acid which remained (1906) unidentified. A curious difference between pinene and limonene nitrosochlorides in action with magnesium methyl iodide revealed itself (1905—6), for while the bimolecular pinene nitrosochloride yields two unimolecular compounds (1905), in one of which the chlorine atom survives, the two products from limonene nitrosochlorides (1906) are still bimolecular and isomeric, having lost one atomic proportion of oxygen. At the same time it was found that the process of reducing nitrosopinene to pinylamine may be carried to the further stage of dihydropinylamine, identical with the base arising from the oxime of pinocamphone on reduction (1906).

The second main division of Tilden's researches has been summarised in contributions to the Philosophical Transactions of the Royal Society, and arose from the conflict of opinion regarding the atomic weights of nickel and cobalt; it deals with the specific heat of metals, and the relation of specific heat to atomic weight. Tilden's original purpose, conceived about 1895, developed into the wider field of testing further the law of Dulong and Petit, and the opening experiments on cobalt and nickel were subsequently extended to gold, platinum, copper, iron, silver and aluminium. Great care was exercised in purifying the metals initially used, and a long series of experiments with them was made in the Joly differential steam-calorimeter. As the inquiry widened, however, the range of temperature was extended through that of solid carbon dioxide to the boiling point of oxygen, and the research owed much to the patient and assiduous co-operation of Mr. Sidney Young. It was found that the influence of temperature effects great alterations in the specific heat of different metals, and the assumption of a constant atomic heat at the absolute zero had to be abandoned. The concluding section of this inquiry, published in 1904, was directed to testing the validity of Neumann's law which assumes that when an atom undergoes chemical combination it retains that capacity for heat which is displayed in the elemental state, and for this purpose the tellurides of nickel, tin and silver were examined, along with silver–aluminium alloy. The results were interpreted as indicating that Neumann's law may be regarded as approximately valid for specific heats at all temperatures, and that specific heat is not a measure of work done in separating the molecules of a substance, but is determined almost entirely by the nature of the atoms composing the physical molecules. A final summary of contemporary knowledge relating to this field was made the subject of Tilden's second presidential address to the Chemical Society (1905).

In this division also must be grouped the paper on "Molecular Weight and Formula of Phosphoric Anhydride and of Metaphosphoric Acid" (1896), in which it was shown that these familiar derivatives of phosphorus are P_4O_{10} and $H_2P_2O_6$. Thus it will be recognised that the scope of his research was wide and that, in common with those of other active workers at a time when boundaries between the organic and inorganic branches were less rigid, and when physical chemistry was unknown, his interests embraced a variety of topics. This was reflected in the freedom he ungrudgingly gave to his staff and students in choosing their own subjects for research, leading to a great diversity in production from the department under his control. Until a late period of his life he remained unreconciled to such divisions of classification and technique as had then inevitably asserted themselves, and he continued to be a true chemical philosopher to the end. His earlier books, "Introduction to Chemical Philosophy" (1876), "A Manual of Chemistry" (1896), and "A Short History of the Progress of Scientific Chemistry" (1899), were characteristic of this attitude, which appeared also in the Cannizzaro Memorial Lecture delivered on June 26th, 1912, and the first presidential address of March, 1904, when he reviewed the state of knowledge and theory during the early years of the Chemical Society. A chemist with these tastes, present at scientific meetings with regularity since his first attendence in 1862, and recalling a lecture by Berthelot on "Synthetic Methods in Organic Chemistry" (June 4th, 1863), had indeed a mine of material upon which to draw.

A dispassionate survey of Sir William Tilden's life leads easily to the conclusion that he was a self-made man in the finest interpretation of the title: and the product was fine. Hampered by early disadvantages, he overcame them by determination and industry. Without useful friends in early life, he made them; and made them by those qualities of character that make the best. Threatened by submergence in a humdrum occupation, he looked below the surface of his materials and found that which enabled him to rise high above their surface, and to vivify the materials themselves. Becoming a teacher through the chance by which science-teaching is almost the only shelter for the potential investigator, he remained faithful to the calling which gave him that shelter, continuing as an active and conscientious teacher during forty-six years. Imbued with a profound interest in all aspects of chemistry, historical, human, and philosophical, but free from ostentation or flamboyance, his teaching prospered more by graceful and accurate presentation than by personal magnetism. Drift of circumstances involved him in two pioneer movements, the founda-

tion of a modern side to a great public school, and the construction of a science-school which became a great university: both movements were substantially furthered by his personality and persistence. These qualities he devoted also to the service of chemistry as a profession, in a degree which few chemists have attained, his association with the Chemical Society and the Institute of Chemistry bearing witness to this loyalty. Throughout a laborious career, oppressed by early difficulties and clouded at times by domestic affliction, he cherished a fine appreciation of the graces which life offers, and enjoyed their consolations with evident gratitude. Into the common dealings of every day there was woven that shade of dignity which has now become old-fashioned, but remains precious; it was entirely unaffected, and untouched by vanity or coldness; because, underlying it, as his intimates were well aware, ran a strong current of generosity and affection.

M. O. F.

WILLIAM CARLETON WILLIAMS.

BORN AUGUST 17TH, 1850; DIED MAY 25TH, 1927.

TWENTY-THREE years ago W. Carleton Williams retired from the Professorship of Chemistry in the University College, Sheffield, a position to which he was appointed in 1883, in succession to Carnelley, the first Professor of Chemistry in the Firth College, which subsequently became the University College, Sheffield.

Firth College was founded by the munificence of Mark Firth, and was opened by Prince Leopold in 1879. Its history, like that of other similar institutions of that period, was, during the first decade of its existence, an unbroken struggle against financial difficulties and restricted conditions. The Technical Education Act of 1889, and the beginning of the Government grants to University Colleges to enable them to develop also on the side of the humanities and pure science, combined to mitigate the severity of the struggle. The next decade witnessed the development of a movement for co-operation between Firth College, the Medical School, which was founded in 1828, and the Technical School, a rate-supported institution. The incorporation of these three bodies, and the raising of an endowment fund, as a memorial of the visit of Queen Victoria to Sheffield, in the year of the Diamond Jubilee, resulted in the grant of a Charter to the new University College in May 1897. The breaking up of the Victoria University, with the immediate result of the creation of the Universities of Liverpool and of Manchester, and later that of Leeds, resulted, naturally, in the desire for a similar recognition and status on behalf of the University College in Sheffield.

W. Carleton Williams

[To face p. 3202.]

In addition to the funds already subscribed for buildings, a call was made for an endowment fund of £100,000 to secure the desired recognition. The successful issue of this effort was the grant, in May 1904, of a University Charter.

Carleton Williams' twenty-one years' tenure of the Firth Chair of Chemistry were momentous years in the development of the College; he not only shared to the full in the anxieties and activities of that period, but contributed generously to the funds raised from time to time, and to the University Endowment Fund he subscribed a year's salary.

The advancement of the College to University status and the approaching completion of the Chemical Laboratory in the new buildings, with the design and arrangement of which he had busied himself, appeared to Williams a suitable opportunity to put into effect his contemplated resignation, thus giving his successor a perfectly free hand. The College Council on receiving his resignation passed the following resolution: "That in accepting with great regret the resignation of Professor W. Carleton Williams of the Firth Chair of Chemistry, the Council desires to place on record its appreciation of the valuable services which he has rendered to the College during his 21 years' connection with the College."

Carleton Williams received his chemical training at the Owens College, Manchester, under Dr. Roscoe (later Sir Henry), entering the College in 1866, in his seventeenth year. His course of study was crowned by the award, in 1871, of the Dalton Chemical Scholarship, for which he presented an account of the results of an investigation on the oxychlorides of antimony (*Mem. Manchester Phil. Soc.*, 1872, 3; 1876, 61). In the same year he was elected an Associate of Owens College. As Dalton Scholar, in accordance with the tradition of those days, Williams went to Germany, where he continued his studies, working first in Bunsen's laboratory at the University of Heidelberg and then, in the second year, at the University of Bonn, where Kekulé directed the Chemical Department. In Bonn he devoted himself to extending his knowledge of organic chemistry, and an outcome of this period was the publication in the *Berichte*, "Ueber Terebinsäure und Pyroterebinsäure" (1873, **6**, 1094). Amongst his fellow students at Bonn were van 't Hoff, Claisen, Königs, Bernthsen, and Wallach, who became *Privat-docent*, then Extra-ordinary Professor, and later Professor of Chemistry in the University of Göttingen.

Returning to Manchester in 1873, Williams was appointed Demonstrator in Chemistry, thus commencing his teaching career in the first session in the new buildings, to which the Owens College had been transferred from the original quarters in Quay Street.

At this time the staff of the Chemical Department consisted, in addition to Professor Roscoe, of C. Schorlemmer, as Lecturer in Organic Chemistry, W. Dittmar as Lecturer in Chemistry, and W. Carleton Williams and H. Grimshaw, Demonstrators. The ten years spent at Owens College were years in which, with laboratory teaching, day and evening classes, and tutorial classes, "full-time" was literally interpreted, and time for research was only to be secured in snatches and by dedicating portions of the vacation to such work.

During this period Williams published the following papers: The Derivatives of Di*iso*butyl (J., 1877, **31**, 541; 1879, **35**, 541); Stannic Arsenate (*Mem. Manchester Phil. Soc.*, 1876, 67); On some Compounds of Antimony Pentachloride with Ethyl Alcohol and with Ether (J., 1876, **29**, 463). With Carnelley he conducted an investigation, the results of which were communicated to this Society, *viz.*: On the Determination of High Boiling Points (J., 1878, **33**, 281); On the Boiling Points of Certain Metals and Metallic Salts (J., 1879, **35**, 563); The Melting and Boiling Points of Certain Inorganic Substances (J., 1880, **37**, 125); and in conjunction with the writer a paper "*Ueber die Bestimmung des specifischen Brechungs-Vermögens festen Körper in ihren Lösungen*" (*Ber.*, 1881, **14**, 2549), which formed part of the report of the British Association Committee on Refraction of Solids: Determining Specific Refractions of Solids from their Solutions.

In the course of an investigation on the sulphides of phosphorus Williams met with a serious accident due to an explosion, in which he was badly burnt on the face, head and hands; fortunately the eyes were not permanently affected.

After the granting of the Charter creating the Victoria University, Williams was made a Lecturer in Chemistry in the University, and in recognition of his standing as an Associate of Owens College, was admitted to the degree of B.Sc. at the first graduation ceremony of the University in 1882.

The translation of Lothar Meyer's "*Die Modernen Theorien der Chemie*," undertaken by Williams in association with the writer, was published in 1888, and was followed in 1892 by the translation of Lothar Meyer's "*Grundzüge der theoretischen Chemie.*"

At Sheffield, Williams devoted himself to teaching and the development of his department. An epidemic of lead poisoning in Sheffield led to an investigation of the action of water on lead, and to the volume published to commemorate the incorporation of the University College at Sheffield he contributed an account of his extensive examination of the distribution of carbonic acid in the air.

Further, the results of his examination of methods for the deter-

mination of zinc formed part of the Report of the British Association Committee on Electrolytic Methods of Quantitative Analysis, published in 1898.

On leaving Sheffield Williams moved to the south and settled at Goring-on-Thames, where Mrs. Williams and he found congenial occupation in tending and developing their garden. Archæology claimed his interest, and he became a member of the British Archæological Association and of the Berkshire Archæological Society, the meetings of which and the Summer Congress he attended regularly. In fact a fortnight before his death he took part in an excursion of the Association to Dunstable. He served for some years on the Council of the British Archæological Association.

In his earlier days Williams found considerable pleasure and recreation in tramping, and thus acquired an intimate knowledge of the Lake District, North Wales and other parts of the country, and in like manner gained an acquaintance with the Rhineland, Switzerland, the Bavarian Alps, the Dolomites and other districts in Europe. The writer retains pleasant recollections of many such tramps, made in his company. Travel always appealed to Williams and he had visited most of the capital towns of Europe, and also Canada and the United States of America. From early manhood he was liable to attacks of gout and it was during one of these attacks that he passed away on May 25th of this year.

William Carleton Williams was born at Salford on August 17th, 1850; in 1883 he married Miss S. E. Andrews, who with their daughter, Ethel Carleton, survives him. Miss Carleton Williams graduated in the History Schools at Oxford and is the authoress of several clever and interesting books dealing with her experiences and travels.

The Jubilee of Williams's Fellowship of the Chemical Society occurred three years ago, for he was elected in 1874; he served for many years on the staff of Abstractors for the Journal; in 1894 he was elected a Fellow of the Institute of Chemistry, and since 1877 was a Member of the British Association. Under his will the Chemical Society is a beneficiary, as are also the Faculty of Science of the University of Sheffield, the Chemical Department of the University of Manchester, and the Benevolent Fund of the Institute of Chemistry.

P. Phillips Bedson.

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FORMULA INDEX.

THE following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus C_1 group, C_2 group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Salts are placed with the compounds from which they are derived. The chlorides, bromides, iodides, and cyanides of quaternary ammonium bases, however, are registered as group-substances.

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CH_4ON_4 Carbohydrazide, reactions of (BROWN, PICKERING, and WILSON), 107.

C_2 Group.

C_2H_2 Acetylene, action of nitric acid on (MCKIE), 962.

C_2H_4 Ethylene, action of nitric acid on (MCKIE), 962.

2 II

$C_2H_2O_4$ Oxalic acid, formation of, from sugars (CHALLENGER, SUBRAMANIAM, and WALKER), 200; (WALKER, SUBRAMANIAM, and CHALLENGER), 3044.

$C_2H_4O_2$ Acetic acid, purification of (ORTON and BRADFIELD), 983; equilibria of, with its copper and lead salts and water (SANDVED), 2967.

C_2H_5I Ethyl iodide, preparation of (JONES and GREEN), 928.

C_2H_6O Ethyl alcohol, surface tension of (MILLS and ROBINSON), 1823; dehydration of (SMITH), 1288; effect of temperature on solubility in aqueous mixtures of (WRIGHT), 1334; determination of water in (SMITH), 1284.

2 III

C_2HOCl_3 Chloral, action of, with arylhydrazines (CHATTAWAY and BENNETT), 2850; condensation of *p*-hydroxybenzoic acid with (CHATTAWAY and PRATS), 685; condensation of, with phenol (CHATTAWAY and MORRIS), 2013.

$C_2H_2O_6Mo$ Oxalomolybdous acid, barium salt (JAMES and WARDLAW), 2152.

2 IV

$C_2H_2O_2ClI$ Chloroiodoacetic acid, resolution of, and its salts (McMATH and READ), 537.

$C_2H_8ON_2Cu$ Ethylenediamminocupric hydroxide, hydrated sulphite of (MORGAN and BURSTALL), 1266.

C_3 Group.

C_3O_2 Carbon suboxide, properties of (EDWARDS and WILLIAMS), 855.

3 II

C_3H_6O Acetone, autocatalytic reaction between iodine and (DAWSON), 458.

$C_3H_6O_2$ Methyl acetate, vapour pressures of mixtures of, with water and with sucrose and water (McKEOWN and STOWELL), 97.

$C_3H_6O_3$ *dl*-Glyceraldehyde, preparation and properties of (REEVES), 2477.

C_3H_9N Trimethylamine, action of, with benzyl and nitrobenzyl chlorides (McCOMBIE, SCARBOROUGH, and SMITH), 802.

3 III

C_3H_3OBr α-Bromoacraldehyde (FARMER and HEALEY), 1066.

$C_3H_9N_2Br$ β-Bromo-αγ-diaminopropane, complex nickel salts of (MANN), 2912.

$C_3H_8N_2S$ *S*-Ethylthiosemicarbazide, dihydrochloride of (BAIRD, BURNS, and WILSON), 2529.

$C_3H_{10}ON_2$ αγ-Diamino*iso*propyl alcohol, complex nickel salts of (MANN), 2913.

3 IV

$C_3H_4O_3N_2S$ Glyoxaline-2-sulphonic acid, and its barium salt (BARNES and PYMAN), 2712.

$C_3H_9ClI_2Hg_2$ Substance, from mercuric chloride and magnesium methyl iodide (HENRY and SHARP), 1949.

$C_3H_{11}N_3Cl_4Pt$ Trichlorotriaminopropaneplatinic chloride (MANN), 1231.

$C_3H_{12}N_3Cl_5Pt$ Tetrachloro(triaminopropanehydrochloride)platinum (MANN), 1229.

3 V

$C_3H_{10}ONCl_4Mo$ Trimethylammonium molybdenyl tetrachloride (JAMES and WARDLAW), 2151.

C_4 Group.

$C_4H_6O_3$ Acetic anhydride, action of bromine on (ORTON, WATSON, and HUGHES), 2458; (WATSON), 3065; estimation of, in acetic acid (ORTON and BRADFIELD), 983.

$C_4H_6O_6$ Dihydroxytartaric acid, action of halogenated phenylhydrazines on (CHATTAWAY and HUMPHREY), 1323; action of tolylhydrazines on (CHATTAWAY and HUMPHREY), 2793.

$C_4H_8O_2$ Ethyl acetate, hydrolysis of (DAWSON and LOWSON), 2107, 2444.

$C_4H_{10}O$ Ethyl ether, viscosity of, at low temperatures (ARCHIBALD and URE), 610; propagation of flame in mixtures of air and (WHITE), 498; action of, on silicon tetrachloride (KIPPING and MURRAY), 2734.

$C_4H_{12}N_2$ β-Methyltrimethylenediamine, dihydrohalides and complex salts of (MANN), 2916.

4 III

$C_4H_4O_2Cl_2$ Succinylchloride, surface tension and density of (GARNER and SUGDEN), 2880.

$C_4H_4O_5Hg_3$ Substance, from heating mercuric acetate and sodium acetate (MARSH and STRUTHERS), 2659.

$C_4H_6O_6Cu$ Cupriglycollic acid, sodium salt (WARK), 1757.

$C_4H_6O_2S_2$ β-Dithian dioxide (BELL and BENNETT), 1801.

$C_4H_9N_3S$ *S*-Allylthiosemicarbazide, dihydrochloride of (BAIRD, BURNS, and WILSON), 2529.

$C_4H_{10}OS$ Methyl γ-hydroxypropyl sulphide (BENNETT and HOCK), 2498.

$C_4H_{10}O_2S_2$ Dimethylethylene disulphoxides (BELL and BENNETT), 1803.

$C_4H_{10}O_3S$ α-Methylpropanesulphonic acid, and its salts (EVANS, MABBOTT, and TURNER), 1167.

$C_4H_{10}NCl$ β-Chlorodimethylethylamine, picrate of (HANHART and INGOLD), 1013.

$C_4H_{11}N_3S$ *S*-Propylthiosemicarbazide, dihydrochloride of (BAIRD, BURNS, and WILSON), 2529.

4 IV

$C_4H_5ON_2Br$ Bromohydroxymethylglyoxaline, and its hydrochloride (GRINDLEY and PYMAN), 3131.

$C_4H_5OCl_2Br$ αβ-Dichloro-β-bromovinyl ethyl ether (SMITH), 1100.

$C_4H_5OCl_2Br_3$ αβ-Dichloro-αββ-tribromodiethyl ether (SMITH), 1101.

C_4H_6ONCl γ-Chloro-α-hydroxy-*n*-butyronitrile (CRAWFORD and KENYON), 400.

$C_4H_6O_2N_2S$ Methylglyoxaline-2-sulphinic acid (BALABAN and KING), 1871.

$C_4H_6O_3N_2S$ Methylglyoxaline-2-sulphonic acid, and its salts (BALABAN and KING), 1872.

4(5)-Methylglyoxaline-5(4)-sulphonic acid, and its salts (BARNES and PYMAN), 2713.

$C_4H_9O_4SNa$ Sodium *sec.*-butyl sulphate (EVANS, MABBOTT, and TURNER), 1167.

$C_4H_{16}ON_4Cu$ Bisethylenediamminocupric hydroxide, salts of (MORGAN and BURSTALL), 1264.

C_5 Group.

$C_5H_{11}N$ Piperidine, use of, as an alkaline buffer (PRIDEAUX and GILBERT), 2164; as a reagent for halogenonitro-compounds (LE FÈVRE and TURNER), 1113.

$C_5H_{13}N$ Dimethyl-*n*-propylamine, and its picrate (HANHART and INGOLD), 1007, 1019.

5 III

$C_5H_5O_2Br$ Bromo-β-vinylacrylic acid (FARMER and HEALEY), 1063.

$C_5H_4O_2Br_2$ Dibromovinylacrylic acid (FARMER and HEALEY), 1062.

$C_5H_8ON_2$ 1-Methyl-2-hydroxymethylglyoxaline, and its picrate (GRINDLEY and PYMAN), 3135.

C_5H_8OS Penthian-4-one (BENNETT and SCORAH), 198.

$C_5H_{10}O_2N_4$ Diacetyl δ-aminosemicarbazone (BROWN, PICKERING, and WILSON), 110.

$C_5H_{13}N_3S$ *S*-Butylthiosemicarbazide, dihydrochloride of (BAIRD, BURNS, and WILSON), 2530.

5 IV

$C_5H_6O_2N_2S$ 2-Thiolmethylglyoxalinecarboxylic acid (BALABAN and KING), 1865.

C_5H_9ONS Penthian-4-one oxime (BENNETT and SCORAH), 199.

5 V

$C_5H_5O_2N_2SAu$ 2-Aurothiolmethylglyoxalinecarboxylic acid (BALABAN and KING), 1870.

$C_5H_8O_2NCl_2Mo$ Pyridinium molybdenum dioxydichloride (JAMES and WARDLAW), 2153.

$C_5H_{11}O_4N_2Cl_2Pt$ Chloro-oxalatotriaminopropaneplatinic chloride (MANN), 1232.

$C_5H_{13}O_4N_2Cl_4Pt$ Tetrachloro(triaminopropanehydrogenoxalate)platinum (MANN), 1231.

5 VI

$C_5H_5O_2N_2ClSHg$ 2-Chloromercurithiolmethylglyoxalinecarboxylic acid (BALABAN and KING), 1871.

C_6 Group.

C_6H_6 Benzene, adsorption of vapour of, by glass, quartz, or platinum (LENHER), 272; partition of hydrochloric acid between water and (KNIGHT and HINSHELWOOD), 466.

$\Delta^{\alpha\epsilon}$-Hexadien-γ-in (FARMER, LAROIA, SWITZ, and THORPE), 2948.

C_6H_8 Hexatriene, structure and behaviour of (FARMER, LAROIA, SWITZ, and THORPE), 2937.

C_6H_{12} *cyclo*Hexane, photobromination of (WOOD and RIDEAL), 2466.

6 II

$C_6H_4O_2$ *p*-Benzoquinone, surface tension and density of (GARNER and SUGDEN), 2880.

C_6H_5Cl Benzyl chloride, action of trimethylamine with (MCCOMBIE, SCARBOROUGH, and SMITH), 802.

C_6H_6O Phenol, condensation of, with chloral (CHATTAWAY and MORRIS), 2013.

$C_6H_6O_2$ Quinol, crystal structure of (CASPARI), 1093.

Resorcinol, condensation of, with cinnamic acid (ELLISON), 1720.

$C_6H_6O_3$ Pyrogallol, condensation of, with cinnamic acid (ELLISON), 1720.

C_6H_7N Aniline, influence of salts on solubility of, in water (GLASSTONE, BRIDGMAN, and HODGSON), 635.

C_6H_7Br Bromohexatrienes (FARMER, LAROIA, SWITZ, and THORPE), 2948.

$C_6H_8O_7$ Citric acid, formation of, from sugars (CHALLENGER, SUBRAMANIAM, and WALKER), 200; (WALKER, SUBRAMANIAM, and CHALLENGER), 3044.

$C_6H_8Br_2$ Dibromohexadienes (FARMER, LAROIA, SWITZ, and THORPE), 2949.

$C_6H_8Br_4$ $\alpha\beta\gamma\delta$-Tetrabromo-Δ^{ϵ}-hexene (FARMER, LAROIA, SWITZ, and THORPE), 2948.

$C_6H_9Br_3$ Tribromohexene (FARMER, LAROIA, SWITZ, and THORPE), 2947.

$C_6H_{10}O_2$ γ-Ethoxycrotonaldehyde (FARMER, LAROIA, SWITZ, and THORPE), 2952.

$C_6H_{10}O_3$ Ethyl acetoacetate, action of, with distyryl ketones (HEILBRON and HILL), 918.

$C_6H_{10}O_8$ Mucic acids, salts (PATTERSON and FULTON), 50.

$C_6H_{10}N_2$ 1:2:3-Trimethylglyoxaline, salts of (GRINDLEY and PYMAN), 3134.

$C_6H_{12}O_2$ Caproic acid, poisoning of charcoal surfaces with (WRIGHT), 2325.

$C_6H_{12}O_6$ Dextrose, mutarotation of, in aqueous alcohols (RICHARDS, FAULKNER, and LOWRY), 1733.

Galactose, structure of (HAWORTH, HIRST, and JONES), 2428.

Lævulose, structure of (HAWORTH, HIRST, and LEARNER), 1040.

$C_6H_{14}O_2$ *s*-Divinylglycol (FARMER, LAROIA, SWITZ, and THORPE), 2946.

$C_6H_{14}O_6$ Dimethyl γ-mannonolactone (GOODYEAR and HAWORTH), 3143.

$C_6H_{15}N$ Dimethyl*iso*butylamine, and its picrate (HANHART and INGOLD), 1017.

$C_6H_{16}N_2$ β-Aminotriethylamine, complex nickel salts of (MANN), 2910.

Dimethylethylethylenediamine, dipicrate of (HANHART and INGOLD), 1010.

6 III

$C_6H_4O_2S$ Thionylpyrocatechol (GREEN), 501.

$C_6H_4N_6Fe$ Hydroferrocyanic acid, calcium and sodium salts, equilibrium of water and (FARROW), 1153; potassium salt, solubility of, in water (VALLANCE), 1328.

C_6H_5OCl *m*-Chlorophenol, Reimer–Tiemann reaction with (HODGSON and JENKINSON), 1740.

$C_6H_5O_3N$ *o*-Nitrophenol, iodination of (HODGSON), 1141.

$C_6H_6O_3N_2$ 3-Nitro-2-aminophenol (KING), 1058.

$C_6H_7O_2Br$ Bromosorbic acid (FARMER and HEALEY), 1064.

Methyl bromo-*p*-vinylacrylate (FARMER and HEALEY), 1063.

C_6H_7NS *o*-Aminothiophenol, condensation of, with $\alpha\beta$-unsaturated acids (MILLS and WHITWORTH), 2738.

$C_6H_8O_2Br_2$ Methyl β-vinylacrylate (FARMER and HEALEY), 1062.

$C_6H_{10}ON_2$ Dimethylhydroxymethylglyoxalines, and their salts (GRINDLEY and PYMAN), 3132.

$C_6H_{10}O_6Cu$ Cuprilactic acid, sodium salt (WARK), 1757.

$C_6H_{10}N_2S$ 2-Ethylthiolmethylglyoxaline, and its salts (BALABAN and KING), 1866.

$C_6H_{12}O_4N_2$ *l*-Dimethoxysuccinamide (HAWORTH and JONES), 2352.

$C_6H_{13}ON$ β-Hydroxylamino-$\beta\gamma$-dimethyl-$\Delta\gamma$-butene, hydrochloride of (EARL and KENNER), 2142.

4-Hydroxy-1-methylpiperidine, and its salts (MILLS, PARKIN, and WARD), 2622.

$C_6H_{13}O_4N$ Hydroxydimethoxybutyramide (AVERY, HAWORTH, and HIRST), 2313.

$C_6H_{13}N_2S$ Acetone *s*-ethylthiosemicarbazone (BAIRD, BURNS, and WILSON), 2529.

$C_6H_{14}NCl$ β-Chlorodimethyldiethylamine, picrate of (HANHART and INGOLD), 1014.

$C_6H_{15}ON$ β-Hydroxydimethyldiethylamine, picrate of (HANHART and INGOLD), 1013.

$C_6H_{19}O_3N_6$ Picratopentamminocobaltic hydroxide, picrates of (DUFF and BILLS), 2371.

6 IV

$C_6HO_4Cl_5S_2$ *s*-Trichlorobenzenedisulphonyl chloride (DAVIES and POWELL), 1124.

$C_6H_2O_7N_3I$ 3-Iodo-2:4:6-trinitrophenol (HODGSON and MOORE), 635.

$C_6H_3O_2NCl_2$ 3:5-Dichloro-4-nitrosophenol[-quinone-4-oxime] (HODGSON and WIGNALL), 2219.

$C_6H_3O_3NCl_2$ 3:5-Dichloronitrophenols (HODGSON and WIGNALL), 2218.

$C_6H_3O_5N_2I$ 3-Iododinitrophenols, and their silver salts (HODGSON and MOORE), 634.

$C_6H_3O_6Cl_3S$ *s*-Trichlorobenzenedisulphonic acid, and its salts (DAVIES and POWELL), 1124.

$C_6H_4O_2NCl$ Nitrobenzyl chloride, action of trimethylamine with (MCCOMBIE, SCARBOROUGH, and SMITH), 802.

$C_6H_4O_2NI$ 3-Iodonitrophenols, and their salts (HODGSON and MOORE), 632.

$C_6H_4O_4Cl_2S_2$ Dichlorothionylquinol (GREEN), 502.

$C_6H_4O_6Cl_2S_2$ 1:3-Dichlorobenzene-4:6-disulphonic acid, and its salts (DAVIES and POOLE), 1122.

$C_6H_5ONCl_2$ 3:5-Dichloroaminophenols (HODGSON and WIGNALL), 2218.

$C_6H_5O_2BrSe$ Bromobenzene-*p*-seleninic acid (PORRITT), 29.

$C_6H_5O_6NHg_5$ Substance, from mercuretin and ammonia (MARSH and STRUTHERS), 2660.

$C_6H_7O_2N_2Br$ α-Bromomuconamides (FARMER and DUFFIN), 408.

$C_6H_8O_2NCl$ γ-Chloro-α-cyanopropyl benzoate (CRAWFORD and KENYON), 400.

$C_6H_9O_4N_2As$ 3:5-Diamino-2-hydroxyphenylarsinic acid (KING), 1057.

$C_6H_{11}ON_3S$ Penthian-4-one semicarbazone (BENNETT and SCORAH), 199.

$C_6H_{11}OIS$ Penthianonemethylsulphonium iodide (BENNETT and SCORAH), 200.

$C_6H_{13}O_2N_3S$ Thiodipropiondiamide (BENNETT and SCORAH), 196.

$C_6H_{15}NClI$ β-Chlorodimethyldiethylammonium iodide (HANHART and INGOLD), 1014.

6 V

$C_6H_5O_4N_2Cl_3S_2$ *s*-Trichlorobenzenedisulphonamide (DAVIES and POOLE), 1124.

$C_6H_{20}ON_2Cl_5Mo$ Ditrimethylammonium molybdenyl pentachloride (JAMES and WARDLAW), 2148.

C_7 Group.

$C_7H_6O_2$ Benzoic acid, heats of combustion of salicylic acid and (BERNER), 338; equilibrium of sulphur with (HAMMICK and HOLT), 493; nitration of (COOPER and INGOLD), 840.

Toluquinone, surface tension and density of (GARNER and SUGDEN), 2880.

$C_7H_6O_3$ *p*-Hydroxybenzoic acid, condensation of chloral with (CHATTAWAY and PRATS), 685.

Salicylic acid, heats of combustion of benzoic acid and (BERNER), 338; copper salt, transport numbers of (HAMER and BURY), 333; molybdenyl salts, isomeric (WARDLAW and WORMELL), 137.

$C_7H_8O_2$ ω-Methoxy-5-methylfurfural (HAWORTH, HIRST, and NICHOLSON), 1524.

$C_7H_8O_4$ ω-Methoxy-5-methylfuran-2-carboxylic acid (HAWORTH, HIRST, and NICHOLSON), 1525.

$C_7H_{17}N$ Dimethylethyl-*n*-propylamine, salts of (HANHART and INGOLD), 1006.

Trimethyl*iso*butylamine, picrate of (HANHART and INGOLD), 1017.

7 III

$C_7H_3OCl_3$ 2:3:5-Trichlorobenzaldehyde (HODGSON and BEARD), 2382.

$C_7H_3O_8N_3$ 2:4:6-Trinitro-3-hydroxybenzaldehyde (HODGSON and BEARD), 2379.

$C_7H_4OBr_2$ 3:4-Dibromobenzaldehyde (HODGSON and BEARD), 26.

$C_7H_4OI_2$ 3:4-Di-iodobenzaldehyde (HODGSON and BEARD), 27.

$C_7H_4O_2Br_4$ Substance, from bromine and dimethylpyrone (COLLIE and KLEIN), 2163.

$C_7H_4O_6N_2$ Dinitrohydroxybenzaldehydes, and their salts (HODGSON and BEARD), 2378.

C_7H_5OCl Benzoyl chloride, nitration of (COOPER and INGOLD), 839.

$C_7H_5O_2Cl$ Chlorohydroxybenzaldehydes (HODGSON and JENKINSON), 1740.

$C_7H_5O_2I$ Iodohydroxybenzaldehydes (HODGSON and JENKINSON), 3043.

$C_7H_5O_2Cl$ 2-Chloro-4-hydroxybenzoic acid (HODGSON and JENKINSON), 1742.

$C_7H_5O_3Br$ Bromohydroxybenzoic acids (HODGSON and JENKINSON), 3042.

$C_7H_5O_3I$ Iodohydroxybenzoic acids (HODGSON and JENKINSON), 3043.

C_7H_5NSe Benzselenazole (CLARK), 2806.

$C_7H_6O_2Br_2$ Substance, from heating $C_{14}H_{17}O_4Br_3$ with water (COLLIE and KLEIN), 2162.

$C_7H_6O_3N_2$ Nitrobenzaldoximes, and their sulphates (BRADY and WHITEHEAD), 2935.

$C_7H_6O_5N_2$ Dinitro-*p*-cresols (DADSWELL and KENNER), 584.

C_7H_7ON Benzamide, nitration of (COOPER and INGOLD), 841.

C_7H_7OCl *o*-Chloroanisole, nitration of (INGOLD and SMITH), 1691.

C_7H_7OBr *o*-Bromoanisole, nitration of (INGOLD and SMITH), 1694.

C_7H_7OI *o*-Iodoanisole, nitration of (INGOLD and SMITH), 1695.

C_7H_7OK Potassium *m*-tolyloxide, interaction of aliphatic esters with (SMITH), 170.

$C_7H_7O_2Br$ Bromoquinol methyl ethers (IRVINE and SMITH), 74.

$C_7H_7O_2N$ Acetyl-α-furfuraldoxime (BRADY and GOLDSTEIN), 1961.

$C_7H_7O_3N_3$ 3-Nitro-4-aminobenzaldoxime (HODGSON and BEARD), 23.

$C_7H_7O_3Br$ Substance, from bromine and diacetylacetone salts (COLLIE and KLEIN), 2164.

$C_7H_8O_3S$ Toluene-ω-sulphonic acid, nitration of (BOTTOMLEY and ROBINSON), 2786.

$C_7H_8O_2Se$ Tolueneseleninic acids (PORRITT), 29.

$C_7H_8O_3N_2$ *O-p*-Nitrobenzylhydroxylamine, and its hydrochloride (BRADY and KLEIN), 882.

$C_7H_9O_3Br$ Methyl bromosorbate (FARMER and HEALEY), 1064.

$C_7H_9O_2N$ ω-Methoxy-5-methylfurfuraldoxime (HAWORTH, HIRST, and NICHOLSON), 1524.

$C_7H_{10}O_2Br_2$ Methyl dibromosorbate (FARMER and HEALEY), 1064.

$C_7H_{11}O_2N$ ββ-Dimethylglutarimide (SIRCAR), 604.

as-Methylethylsuccinimide (SIRCAR), 1254.

$C_7H_{12}N_2S$ Acetone *S*-allylthiosemicarbazone (BAIRD, BURNS, and WILSON), 2529.

$C_7H_{14}ON_4$ Diacetonecarbohydrazone (BROWN, PICKERING, and WILSON), 108.

$C_7H_{15}O_3N$ Carnitine, constitution of (CRAWFORD and KENYON), 396.

$C_7H_{15}N_2S$ Acetone *S*-propylthiosemicarbazone (BAIRD, BURNS, and WILSON), 2529.

7 IV

$C_7H_3O_4NCl_2$ 2:5-Dichloro-3-nitrobenzoic acid (HODGSON and BEARD), 2381.

$C_7H_3NBr_2S$ 2:5-Dibromophenylthiocarbimide (DYSON, GEORGE, and HUNTER), 443.

$C_7H_4ON_2Br_4$ 2:4:5:6-Tetrabromo-3-aminobenzaldoxime (HODGSON and BEARD), 2427.

$C_7H_4O_3NI$ 4-Iodo-3-nitrobenzaldehyde (HODGSON and BEARD), 25.

C_7H_4NIS Iodophenylthiocarbimides (DYSON, GEORGE, and HUNTER), 443.

$C_7H_5ONBr_2$ 3:4-Dibromobenzaldoxime (HODGSON and BEARD), 26.

$C_7H_5ONI_2$ 3:4-Di-iodobenzaldoxime (HODGSON and BEARD), 27.

$C_7H_5OCl_2I$ Dichloroiodoanisole (INGOLD, SMITH, and VASS), 1249.

$C_7H_5O_2NCl_2$ 2:4-Dichloro-5-nitrotoluene (DADSWELL and KENNER), 585.

$C_7H_5O_2N_2S$ 3-Nitro-1-aminobenzthiazole (DYSON, HUNTER, and MORRIS), 1192.

$C_7H_5O_3NCl_2$ 3:5-Dichloronitroanisoles (HODGSON and WIGNALL), 2219.

$C_7H_5O_3N_2Cl$ 4-Chloro-3-nitrobenzaldoxime (HODGSON and BEARD), 24.

$C_7H_5O_3N_2I$ 4-Iodo-3-nitrobenzaldoxime (HODGSON and BEARD), 25.

$C_7H_5N_2ClS$ 5-Chloro-1-aminobenzthiazole (DYSON, HUNTER, and MORRIS), 1190.

$C_7H_5N_2Br_5S$ 5-Bromo-1-aminobenzthiazole tetrabromide (DYSON, HUNTER, and MORRIS), 1191.

C_7H_6ONCl α-*o*-Chlorobenzaldoxime, sulphate of (BRADY and WHITEHEAD), 2936.

C_7H_6ONI Iodohydroxybenzaldoximes (HODGSON and JENKINSON), 3043.

C_7H_6OClI 4-Chloro-2-iodoanisole (INGOLD, SMITH, and VASS), 1248.

$C_7H_6O_2NCl$ Chlorohydroxybenzaldoxime (HODGSON and JENKINSON), 1740.

3-Chloro-4-nitroanisole (HODGSON and WIGNALL), 2220.

$C_7H_6O_3NI$ 3-Iodonitrophenyl methyl ethers (HODGSON and MOORE), 632.

$C_7H_6N_2Br_2S$ 2:5-Dibromophenylthiocarbamide (DYSON, GEORGE, and HUNTER), 443.

$C_7H_7ONCl_2$ 3:5-Dichloro-4-aminoanisole (HODGSON and WIGNALL), 2219.

$C_7H_7O_2ClS$ Toluene-ω-sulphonyl chloride (BOTTOMLEY and ROBINSON), 2785.

$C_7H_7N_2BrS$ *o*-Bromophenylthiocarbamide (DYSON, GEORGE, and HUNTER), 443.

$C_7H_7N_2IS$ Iodophenylthiocarbamides (DYSON, GEORGE, and HUNTER), 443.

$C_7H_9O_5N_2As$ 2 Hydroxy-4-carbamidophenylarsinic acid, and its salts (KING), 1056.

$C_7H_{10}O_2N_2S$ 2-Ethylthiolmethylglyoxalinecarboxylic acid, and its hydrochlorides (BALABAN and KING), 1867.

$C_7H_{15}ON_2Cl$ γ-Dimethylamino-α-hydroxy-*n*-butyronitrile methochloride, and its salts (CRAWFORD and KENYON), 401.

$C_7H_{16}O_3NCl$ α-Hydroxy-γ-butyrotrimethylbetaine hydrochloride, and its salts (CRAWFORD and KENYON), 401.

7 V

$C_7H_5ONClBr$ Chlorobromobenzaldoximes (HODGSON and BEARD), 25.

C_7H_5ONClI Chloroiodobenzaldoximes (HODGSON and BEARD), 26.

C_7H_5ONBrI Bromoiodobenzaldoximes (HODGSON and BEARD), 26.

$C_7H_5N_2ClBr_2S$ 5-Chloro-1-aminobenzthiazole dibromide (DYSON, HUNTER, and MORRIS), 1190.

$C_7H_5N_2ClBr_6S$ 5-Chloro-1-aminobenzthiazole hexabromide (DYSON, HUNTER, and MORRIS), 1191.

$C_7H_6O_4NClS$ Nitrobenzylsulphonyl chlorides (C. K. and E. H. INGOLD and SHAW), 831.

$C_7H_9O_2N_2SAu$ Ethyl 2-aurothiolmethylglyoxalinecarboxylate (BALABAN and KING), 1869.

7 VI

$C_7H_9O_2N_2ClSHg$ Ethyl 2-chloromercurithiolmethylglyoxalinecarboxylate (BALABAN and KING), 1871.

C_8 Group.

C_8H_{12} αζ-Dimethylhexatriene (FARMER, LAROIA, SWITZ, and THORPE), 2957.

8 II

$C_8H_6O_4$ *iso*Phthalic acid, oxidation of (FARMER and RICHARDSON), 62.

$C_8H_8O_3$ Acetylpyrocatechol (GREEN), 502.

Mandelic acid, cupric salt (WARK), 1754.

$C_8H_{10}O_3$ 2:3-Dimethyl*cyclo*butane-1:4-dicarboxylic anhydride (VOGEL), 1993.

$C_8H_{10}O_4$ 4:5-Dimethoxyresorcinol (CHAPMAN, PERKIN, and ROBINSON), 3031.

4-Hydroxy-2:2-dimethyl*cyclo*penten-3-one-1-carboxylic acids (GIBSON, HARIHARAN, and SIMONSEN), 3013.

Methyl ω-methoxy-5-methylfuran-2-carboxylate (HAWORTH HIRST, and NICHOLSON), 1525.

$C_8H_{12}O_2$ Ethyl Δ^1-*cyclo*pentenecarboxylate (SIRCAR), 1255.

*cyclo*Hexylideneacetic acid, sodium salt (LINSTEAD), 370.

3-Hydroxy*cyclo*hexolacetolactone (ROBINSON and ZAKI), 2411.

$C_8H_{12}O_4$ 2:3-Dimethyl*cyclo*butane-1:4-dicarboxylic acids (VOGEL), 1993.

Methyl Δβ-dihydromuconate (FARMER and DUFFIN), 409.

Methylethylparaconic acid, and its silver salt (SIRCAR), 1258.

*trans-cyclo*Pentane-1-carboxy-2-acetic acid (SIRCAR), 1255.

$C_8H_{12}Br_2$ Dibromo-*s*-dipropenylethylene glycol (FARMER, LAROIA, SWITZ, and THORPE), 2957.

$C_8H_{14}O_2$ β-Methyl-α-ethyl-Δβ-pentenoic acid, and its silver salt (KON and NARAYANAN), 1545.

$C_8H_{14}O_5$ 2:3:4-Trimethyl *l*-arabonolactone (DREW and MACBETH), 778.

Trimethyl arabonolactones (DREW, GOODYEAR, and HAWORTH), 1244.

Trimethyl γ-arabonolactones, oxidation of (HAWORTH, HIRST, and LEARNER), 2432.

Trimethyl xylonolactones (DREW, GOODYEAR, and HAWORTH), 1244.

$C_8H_{16}O_6$ γ-Ethylfructoside (ALLPRESS, HAWORTH, and INKSTER), 1235.

$C_8H_{18}O$ α-Ethoxyhexane (FARMER, LAROIA, SWITZ, and THORPE), 2951.

$C_8H_{20}N_4$ β-Dimethylaminodimethyldiethylamine picrate (HANHART and INGOLD), 1011.

Hexamethylethylenediamine, picrate of (HANHART and INGOLD), 1012.

8 III

$C_8H_3N_3Mo$ Hydromolybdicyanic acid, and its salts (Bucknall and Wardlaw), 2987.

$C_8H_4O_2Cl_2$ Phthalyl chlorides, surface tension and density of (Garner and Sugden), 2881.

$C_8H_4N_2Cl_4$ *αα*-Dichloro-*β*-2:4-dichlorobenzeneazoethylene (Chattaway and Bennett), 2853.

$C_8H_4N_2S$ Cyanophenylthiocarbimides (Dyson, George, and Hunter), 442.

$C_8H_4N_3Mo$ Hydromolybdocyanic acid, salts of (Bucknall and Wardlaw), 2981.

$C_8H_5O_4N_3$ 2:4-Dinitrophenylacetonitrile (Fairbourne and Fawson), 48.

$C_8H_6OCl_2$ 3:4-Dichloroacetophenone (Roberts and Turner), 1855.

$C_8H_6O_3Cl_2$ 3:5-Dichloroanisic acid (Blakey, Jones, and Scarborough), 2868.

$C_8H_6O_5N_2$ *α*-6-Nitro-3:4-methylenedioxybenzaldoxime, sulphate of (Brady and Whitehead), 2937.

$C_8H_6O_6N_2$ Dinitromethoxybenzaldehydes (Hodgson and Beard), 2381.

$C_8H_6O_7N_2$ 2:3-Dinitro-4-methoxybenzoic acid (Dadswell and Kenner), 587.
2:6-Dinitro-3-methoxybenzoic acid (Hodgson and Beard), 2381.

$C_8H_7O_2N$ 2-Hydroxy-5-methoxybenzonitrile (Shinoda), 1984.

$C_8H_7O_2Cl$ 4-Chloro-2-methoxybenzaldehyde (Hodgson and Jenkinson), 1741.

$C_8H_7O_2Br$ Bromomethoxybenzaldehydes (Hodgson and Jenkinson), 3042.

$C_8H_7O_2I$ Iodomethoxybenzaldehydes (Hodgson and Jenkinson), 3043.

$C_8H_7O_3N$ *α*-3:4-Methylenedioxybenzaldoxime, sulphate of (Brady and Whitehead), 2937.

$C_8H_7O_3N_3$ 7-Nitro-6-methoxyindazole (Dadswell and Kenner), 586.

$C_8H_7O_3Cl$ 4-Chloro-2-methoxybenzoic acid (Hodgson and Jenkinson), 1741.

$C_8H_7O_3Br$ Bromomethoxybenzoic acids (Hodgson and Jenkinson), 3042.

$C_8H_7O_3I$ Iodomethoxybenzoic acids (Hodgson and Jenkinson), 3043.

$C_8H_7N_2S$ Cyanophenylthiocarbamides (Dyson, George, and Hunter), 442.

$C_8H_7Cl_2Br$ *α*-2:4-Dichlorophenylethyl bromide (Evans, Mabbott, and Turner), 1165.

$C_8H_8OCl_2$ 2:4-Dichlorophenylmethylcarbinol (Evans, Mabbott, and Turner), 1164.

$C_8H_8O_4N_2$ Dinitro-*β*-phenylethane (Baker and Wilson), 846.

$C_8H_8O_6N_2$ 2:5-Dinitrocreosol (Oxford), 1967.
5:6-Dinitro*iso*creosol (Oxford), 1970.

$C_8H_9O_2N$ Methoxybenzaldoximes, sulphates of (Brady and Whitehead), 2936.
α-Nitro-*β*-phenylethane (Baker and Wilson), 844.
Piperonylmethylamine, and its salts (Malan and Robinson), 2654.

$C_8H_9O_2Cl$ Chlorocreosol (Oxford), 1966.

$C_8H_9O_3N$ 2-Hydroxy-5-methoxybenzaldoxime (Shinoda), 1984.

$C_8H_9O_4N$ 6-Nitro*iso*creosol (Oxford), 1970; (Heap, Jones, and Robinson), 2022.

$C_8H_9O_4N_3$ *p*-Nitrobenzyloxycarbamide (Brady and Klein), 882.

$C_8H_9O_4Br$ Methyl *α*-bromomuconates (Farmer and Duffin), 407.

$C_8H_{10}ON_4$ Benzaldehyde *δ*-aminosemicarbazone (Brown, Pickering, and Wilson), 110.

$C_8H_{10}O_2Se$ Xylene-4-seleninic acids (Porritt), 29.

$C_8H_{10}O_3N_2$ Nitro-4-methoxytoluidines (Dadswell and Kenner), 584.
Nitroso-*N*-*o*-methoxybenzylhydroxylamine (Brady and Bennett), 897.

$C_8H_{10}O_3S$ Phenylethanesulphonic acids, and their salts (Evans, Mabbott, and Turner), 1161.

$C_8H_{10}O_4Br_2$ Methylmuconate dibromides (Farmer and Duffin), 402.

$C_8H_{10}NCl$ Chloro-*m*-2-xylidines (DADSWELL and KENNER), 1106.
$C_8H_{10}NI$ 3-Iododimethylaniline (HODGSON and WIGNALL), 1145.
$C_8H_{11}O_2N$ *trans*-Hexahydrophthalimide (SIRCAR), 1254.
N-*o*-Methoxybenzylhydroxylamine, hydrochloride of (BRADY and BENNETT), 896.
*trans-cyclo*Pentane-1-carboxy-2-acetimide (SIRCAR), 1255.
*cyclo*Pentane*spiro*succinimide (SIRCAR), 1254.
$C_8H_{11}O_2I$ 1-Iodo-2-hydroxy*cyclo*hexylacetic acid γ-lactone (LINSTEAD and MAY), 2572.
$C_8H_{11}O_3N_3$ ω-Methoxy-5-methylfurfural semicarbazone (HAWORTH, HIRST, and NICHOLSON), 1523.
$C_8H_{11}N_3S$ δ-Benzylthiosemicarbazide, and its hydrochloride (BAIRD, BURNS, and WILSON), 2531.
$C_8H_{12}O_2S$ Ethyl penthian-4-one-3-carboxylate (BENNETT and SCORAH), 198.
Ethyl Δ^3-penthien-4-ol-3-carboxylate (BENNETT and SCORAH), 197.
$C_8H_{13}O_2N$ *as*-Diethylsuccinimide (SIRCAR), 1254.
βδ-Methylethylglutarimide (SIRCAR), 604.
$C_8H_{13}O_3N_3$ Δγ-Pentene-*aaε*-tricarboxylamide (FARMER and HEALEY), 1065.
$C_8H_{15}O_3N$ Methylbetaines of 4-hydroxypiperidylacetic acid (MILLS, PARKIN, and WARD), 2623.
$C_8H_{16}O_4N_2$ Dimethoxysuccinomethylamides (HAWORTH and JONES), 2351.
$C_8H_{17}N_3S$ Acetone δ-butylthiosemicarbazone (BAIRD, BURNS, and WILSON), 2530.
$C_8H_{19}N_3S$ δ-Heptylthiosemicarbazide, and its hydrochloride (BAIRD, BURNS, and WILSON), 2533.

8 IV

$C_8H_3N_2Cl_4Br$ *aa*-Dichloro-δ-bromo-β-2:4-dichlorobenzeneazoethylene (CHATTAWAY and BENNETT), 2853.
$C_8H_4N_2Cl_2Br_2$ *aa*-Dichloro-β-2:4-dibromobenzeneazoethylene (CHATTAWAY and BENNETT), 2853.
$C_8H_4N_2Cl_3Br_2$ *aa*-Dichlorochlorobromobenzeneazoethylenes (CHATTAWAY and BENNETT), 2853.
$C_8H_5O_3NCl_2$ 3:4-Dichloro-2-nitroacetophenone (ROBERTS and TURNER), 1855.
$C_8H_5NBr_2S$ 3:5-Dibromo-*o*-tolylthiocarbimide (DYSON, GEORGE, and HUNTER), 444.
$C_8H_5N_3Br_4S$ 1-Amino-5-cyanobenzthiazole tetrabromide (DYSON, HUNTER, and MORRIS), 1189.
$C_8H_5N_3Br_6S$ 1-Amino-5-cyanobenzthiazole hexabromide (DYSON, HUNTER, and MORRIS), 1189.
$C_8H_6O_3N_2Cl_2$ Glyoxylic acid dichlorophenylhydrazone (CHATTAWAY and BENNETT), 2852.
$C_8H_6O_3N_2Br_2$ Glyoxylic acid dibromophenylhydrazone (CHATTAWAY and BENNETT), 2852.
$C_8H_6O_2N_2S$ 3-Nitro-*o*-tolylthiocarbimide (DYSON, GEORGE, and HUNTER), 444.
$C_8H_6O_4NI$ 3-Iodo-6-nitrophenyl acetates (HODGSON and MOORE), 632.
$C_8H_7ONCl_2$ 3:4-Dichloro-2-aminoacetophenone (ROBERTS and TURNER), 1856.
C_8H_7ONS Anisylthiocarbimides (DYSON, GEORGE, and HUNTER), 440.
C_8H_7OClS Chloromethylthiolbenzaldehydes (HODGSON and BEARD), 2427.
$C_8H_7O_3NS$ Nitromethylthiolbenzaldehydes (HODGSON and BEARD), 2425.
C_8H_8ONCl *N*-Chloroacetanilide, action of hydrochloric acid with (SOPER and PRYDE), 2761.
$C_8H_8ON_2S$ 1-Amino-5-methoxybenzthiazole (DYSON, HUNTER, and MORRIS), 1191.

$C_8H_8O_2NCl$ 4-Chloro-2-methoxybenzaldoxime (Hodgson and Jenkinson), 1741. Chloronitro-*m*-xylenes (Dadswell and Kenner), 1106.

$C_8H_8O_2NBr$ Bromomethoxybenzaldoximes (Hodgson and Jenkinson), 3042.

$C_8H_8O_2NI$ Iodomethoxybenzaldoximes (Hodgson and Jenkinson), 3043.

$C_8H_9O_2N_3Cl$ Chlorohydroxybenzaldehyde semicarbazones (Hodgson and Jenkinson), 1741.

$C_8H_9O_2N_3Br$ Bromohydroxybenzaldehyde semicarbazones (Hodgson and Jenkinson), 3041.

$C_8H_9O_2N_3I$ Iodohydroxybenzaldehyde semicarbazones (Hodgson and Jenkinson), 3043.

$C_8H_8O_3NCl$ 3-Chloro-6-nitro-4-methoxytoluene (Dadswell and Kenner), 585.

$C_8H_8O_3N_2S$ Nitromethylthiolbenzaldoximes (Hodgson and Beard), 2425.

C_8H_6NISe Benzselenazole methiodide (Clark), 2806.

$C_8H_8N_2Br_4S$ 1-Amino-5-methylbenzthiazole tetrabromide (Dyson, Hunter, and Morris), 1191.

$C_8H_9ON_2I$ 3-Iodo-4-nitrosodimethylaniline (Hodgson and Wignall), 1145.

$C_8H_9O_2NS$ 3-Nitroso-4-methylthiolbenzyl alcohol (Hodgson and Beard), 2426.

$C_8H_9O_2ClS$ Phenylethanesulphonyl chlorides (Evans, Mabbott, and Turner), 1162.

$C_8H_9O_3NS$ Nitrophenyl β-hydroxyethyl sulphides (Bennett and Berry), 1667.

$C_8H_9O_4NS$ Nitrobenzylmethylsulphones (C. K. and E. H. Ingold and Shaw), 820.

$C_8H_9O_4N_2As$ Hydroxy-1:4-dihydroquinoxaline-6-arsinic acids (Ewins, Newbery, and Stickings), 853.

$C_7H_9O_5NS$ Methyl nitrobenzylsulphonates (C. K. and E. H. Ingold and Shaw), 829.

$C_8H_{10}ON_2S$ 3-Aminomethylthiolbenzaldoximes (Hodgson and Beard), 2427. Anisylthiocarbamides (Dyson, George, and Hunter), 440.

$C_8H_{10}O_4N_2S$ Nitrobenzylsulphonmethylamides (C. K. and E. H. Ingold and Shaw), 824.

$C_8H_{10}O_4N_2Hg$ Ethyl 1-acetoxymercuriglyoxalinecarboxylate (Balaban and King), 1870.

$C_8H_{10}O_6N_2As$ 3-Nitrophenylarsinic acid 4-glycineamide (Ewins, Newbery, and Stickings), 854.

$C_8H_{11}O_2N_2Cl$ Nitro-β-phenylethylammonium chlorides (Goss, Hanhart, and Ingold), 253.

$C_8H_{11}O_4N_2As$ Nitrosoethylaminophenylarsinic acid (Burton and Gibson), 2387.

$C_8H_{12}O_3NAs$ *o*-Ethylaminophenylarsinic acid (Burton and Gibson), 2387.

$C_8H_{15}OBrS$ Tetrahydrothiophen-δ-bromobutylsulphonium bromide, and its picrate (Bennett and Hock), 483.

$C_8H_{15}O_2NBr_2$ 4-Bromoacetoxy-1-methylpiperidine (Mills, Parkin, and Ward), 2625.

$C_8H_{16}O_3NBr$ 4-Hydroxypiperidylacetic acid methobromides (Mills, Parkin, and Ward), 2623.

$C_8H_{17}OBrS$ Tetrahydrothiophen-δ-hydroxybutylsulphonium bromide, and its salts (Bennett and Hock), 482.

8 V

$C_8H_6ONClBr_2$ Chlorodibromoacetanilide (Smith), 1101.

C_8H_6ONClS Chloromethylthiolbenzaldoximes (Hodgson and Beard), 2427.

$C_8H_6ON_2Br_2S$ 1-Amino-5-methoxybenzthiazole dibromide (Dyson, Hunter, and Morris), 1191.

$C_8H_8O_3NClS$ Nitrophenyl β-chloroethyl sulphides (Bennett and Berry), 1672.

$C_8H_8O_3NBrS$ Nitrophenyl β-bromoethyl sulphides (Bennett and Berry), 1672.

$C_8H_8O_2NIS$ Nitrophenyl β-iodoethyl sulphides (Bennett and Berry), 1673.
$C_8H_8O_2NClS$ Nitrophenyl β-chloroethyl sulphoxides (Bennett and Berry), 1672.
$C_8H_8O_2NBrS$ Nitrophenyl β-bromoethyl sulphoxides (Bennett and Berry), 1672.

C_9 Group.

$C_9H_6O_4$ 4:5-Methylenedioxyphthalide (Stevens and Robertson), 2792.
$C_9H_6O_6$ Hydrastic acid, synthesis of (Stevens and Robertson), 2790.
$C_9H_8O_2$ Cinnamic acid, condensation of, with pyrogallol and resorcinol (Ellison), 1720.
$C_9H_8O_3$ Acetophenone-*o*-carboxylic acid (Davies and Poole), 2662.
$C_9H_8O_4$ 5-Carboxy-2-hydroxyacetophenone (Chattaway and Prats), 692.
$C_9H_8O_5$ 6-Hydroxymethylpiperonylic acid, and its silver salt (Stevens and Robertson), 2792.
$C_9H_{10}O_2$ 1:2-Dihydroxyallylbenzenes (Perkin and Trikojus), 1665.
$C_9H_{10}O_3$ *m*-Xylorcylaldehyde (Robertson and Robinson), 2202.
$C_9H_{10}O_5$ 3:6-Dihydroxy-2:4-dimethoxybenzaldehyde (Chapman, Perkin, and Robinson), 3029.
$C_9H_{11}Br$ β-Tolylethyl bromides, isomeric, preparation and hydrolysis of (Shoesmith and Connor), 1768.
$C_9H_{12}O_2$ β-Methoxyphenylethyl alcohols (Shoesmith and Connor), 2233.
$C_9H_{12}O_4$ *cyclo*Pentane*spiro*paraconic acid, and its silver salt (Sircar), 1258.
$C_9H_{12}O_6$ β-Hydroxy-β-ethylbutane-γδδ-tricarboxylic γ-lactone (Sircar), 1258.
$C_9H_{13}N$ Trimethylbenzylamine, picrate of (Goss, Hanhart, and Ingold), 257.
$C_9H_{14}O_2$ ββ-Dipropylacrylic acid, and its silver salt (Kon and May), 1552.
α-Ethyl-Δ^1-*cyclo*pentenylacetic acid, and its silver salt (Kon and Narayanan), 1543.
α-Ethyl*cyclo*pentylideneacetic acid (Kon and Narayanan), 1543.
*cyclo*Heptylideneacetic acid (Kon and May), 1554.
$C_9H_{14}O_3$ Methyl 2:2-dimethyl*cyclo*pentan-3-one-1-carboxylate (Gibson, Hariharan, and Simonsen), 3012.
$C_9H_{14}O_4$ *apo*Fenchocamphoric acid, synthesis of (Short), 961.
$C_9H_{14}O_5$ γ-Acetyl-γ-methylbutane-αβ-dicarboxylic acid (Bhagvat and Simonsen), 87.
α-Keto-ββγγ-tetramethylglutaric hydroxylactone (Rothstein and Shoppee), 533.
$C_9H_{14}O_6$ γ-Mannonolactone-acetone (Goodyear and Haworth), 3143.
$C_9H_{14}N_2$ Aminobenzyldimethylamines, and their hydrochlorides (Stedman), 1905.
$C_9H_{16}O_2$ β-Propylhexoic acid (Kon and May), 1554.
$C_9H_{16}O_3$ 1-Hydroxy-α-ethyl*cyclo*pentaneacetic acid, and its silver salt (Kon and Narayanan), 1543.

9 III

$C_9H_3N_3S$ 2:5-Dicyanophenylthiocarbimide (Dyson, George, and Hunter), 443.
$C_9H_6O_4Cl_2$ ωω-Dichloro-5-carboxy-2-hydroxyacetophenone (Chattaway and Prats), 691.
$C_9H_7O_2N$ Homophthalimide (Sircar), 1255.
$C_9H_8O_5N_2$ β-*O*-Methyl-6-nitro-3:4-methylenedioxybenzaldoxime (Brady and Klein), 894.
$C_9H_8O_7N_2$ Methyl 2:3-dinitro-4-methoxybenzoate (Dadswell and Kenner), 587.
$C_9H_9O_2Cl$ Chlorotropic acids (Kerr), 1947.
$C_9H_9O_6N$ 3-Nitro-2:4-dimethoxybenzoic acid (Dadswell and Kenner), 587.

$C_9H_9NO_3$ *m*-Methoxy-ω-nitrostyrene (SHOESMITH and CONNOR), 2232.
C_9H_9NS Xylylthiocarbimides (DYSON, GEORGE, and HUNTER), 440.
$C_9H_{10}OBr_2$ β-Bromo-2-methoxyphenylethylbromides (SHOESMITH and CONNOR), 2233.
$C_9H_{10}O_3Se$ *o*-Tolylselenoglycollic acid (PORRITT), 28.
$C_9H_{10}O_4N_2$ Methyl *p*-nitrobenzylaminoformate (BAKER), 568.
$C_9H_{10}O_6N_2$ Dinitrohomoveratroles (OXFORD), 1968.
$C_9H_{10}N_2S$ *p*-Dimethylaminophenylthiocarbimide (DYSON, GEORGE, and HUNTER), 442.
$C_9H_{11}ON_3$ 2:3-Dicyano-1-methyl-1-ethyl*cyclo*propane-2-carboxylamide (SIRCAR), 1258.
$C_9H_{11}OBr$ β-*p*-Methoxyphenylethyl bromide (SHOESMITH and CONNOR), 2234.
$C_9H_{11}OI$ Benzyl β-iodoethyl ether (BENNETT and HOCK), 476.
$C_9H_{11}O_2N$ *m*-Methoxyphenylacetaldoxime (SHOESMITH and CONNOR), 2232.
$C_9H_{11}O_2N$ α-Amino-β-hydroxy-α-phenylpropionic acid, and its hydrochloride (KERR), 1946.
$C_9H_{11}O_4N$ 5-Nitro-2:4-dimethoxytoluene (DADSWELL and KENNER), 585.
$C_9H_{11}ClS$ Phenyl γ-chloropropyl sulphide (BENNETT and BERRY), 1680.
$C_9H_{12}ON_4$ Acetophenone-δ-aminosemicarbazone (BROWN, PICKERING, and WILSON), 109.
$C_9H_{12}O_2N_2$ Nitrobenzyldimethylamines, and their hydrochlorides (STEDMAN), 1904.
α-*p*-Nitrophenyl*iso*propylamine, picrate of (BAKER and INGOLD), 264.
$C_9H_{12}O_3Br_2$ Methyl 4:4-dibromo-2:2-dimethyl*cyclo*pentan-3-one-1-carboxylate (GIBSON, HARIHARAN, and SIMONSEN), 3012.
$C_9H_{12}O_3S$ α-Phenylpropanesulphonic acid, and its resolution and salts (EVANS, MABBOTT, and TURNER), 1165.
$C_9H_{12}N_2S$ Xylylthiocarbamides (DYSON, GEORGE, and HUNTER), 440.
$C_9H_{12}ON$ Hydroxybenzyldimethylamines, and their salts (STEDMAN), 1904.
$C_9H_{12}O_2N$ *trans*-Hexahydrohomophthalimide (SIRCAR), 1255.
*cyclo*Hexane*spiro*succinimide (SIRCAR), 1254.
*cyclo*Pentanediacetimide (SIRCAR), 604.
$C_9H_{13}N_2S$ *p*-Dimethylaminophenylthiocarbamide (DYSON, GEORGE, and HUNTER), 442.
δ-α-Phenylethylthiosemicarbazide, and its hydrochloride (BAIRD, BURNS, and WILSON), 2532.
$C_9H_{15}ON$ α-Ethyl-Δ^1-*cyclo*pentenylacetamide (KON and NARAYANAN), 1543.
α-Ethyl*cyclo*pentylideneacetamide (KON and NARAYANAN), 1543.
β-Propyl-Δ^β-hexeno-amide (KON and MAY), 1553.
$C_9H_{15}O_2N$ ββ-Diethylglutarimide (SIRCAR), 604.
$C_9H_{16}ON_4$ Di(methylethyl ketone) carbohydrazone (BROWN, PICKERING, and WILSON), 109.

9 IV

C_9H_7ONS *p*-Acetylphenylthiocarbimide (DYSON, GEORGE, and HUNTER), 442.
$C_9H_8O_2N_2Cl_2$ Methyl glyoxylate 2:4-dichlorophenylhydrazone (CHATTAWAY and BENNETT), 2851.
$C_9H_8O_2N_2Br_2$ Methyl glyoxylate 2:4-dibromophenylhydrazone (CHATTAWAY and BENNETT), 2851.
$C_9H_8O_5N_2S$ 2-Nitro-4-ethoxyphenylthiocarbimide (DYSON, GEORGE, and HUNTER), 444.
C_9H_9ONS Ethoxyphenylthiocarbimides (DYSON, GEORGE, and HUNTER), 441.
4-Ketotetrahydro-1:5-heptabenzthiazine (MILLS and WHITWORTH), 2750.
$C_9H_9O_2NS$ Dimethoxyphenylthiocarbimides (DYSON, GEORGE, and HUNTER), 441.

$C_9H_9O_4NS$ *o*-Nitrophenylthiolpropionic acid (MILLS and WHITWORTH), 2750.
$C_9H_9N_2ClS$ 5-Chloro-1-dimethylaminobenzthiazole (HUNTER and STYLES), 1213.
$C_9H_{10}ONCl$ 2-Chloroaceto-*p*-toluidide, dimorphism of (SCHOFIELD), 2903.
$C_9H_{10}ON_2S$ *p*-Acetylphenylthiocarbamide (DYSON, GEORGE, and HUNTER), 442.
1-Amino-5-ethoxybenzthiazole (DYSON, HUNTER, and MORRIS), 1191.
$C_9H_{10}O_3NBr$ 6-Bromo-β-piperonylethylamine, and its salts (STEVENS), 184.
$C_9H_{10}O_3N_3Cl$ Chloromethoxybenzaldehyde semicarbazones (HODGSON and JENKINSON), 1741, 3042.
$C_9H_{10}O_3N_3Br$ Bromomethoxybenzaldehyde semicarbazones (HODGSON and JENKINSON), 3042.
$C_9H_{10}O_3N_3I$ Iodomethoxybenzaldehyde semicarbazones (HODGSON and JENKINSON), 3043.
$C_9H_{10}O_3NBr$ α-6-Bromo-3:4-dimethoxybenzaldoxime, sulphate of (BRADY and WHITEHEAD), 2936.
$C_9H_{10}O_4NBr$ 6-Bromo-2-nitrohomoveratrole (OXFORD), 1970.
$C_9H_{10}N_2Br_2S$ 1-Dimethylaminobenzthiazole dibromide (HUNTER and STYLES), 1211.
$C_9H_{10}N_2Br_6S$ 1-Dimethylaminobenzthiazole hexabromide (HUNTER and STYLES), 1212.
$C_9H_{11}O_3NS$ *o*-Aminophenylthiolpropionic acid (MILLS and WHITWORTH), 2750.
$C_9H_{11}O_2ClS$ α-Phenylpropanesulphonyl chloride (EVANS, MABBOTT, and TURNER), 1166.
$C_9H_{11}O_3NS$ *p*-Nitrobenzyl β-hydroxyethyl sulphide (BENNETT and BERRY), 1671.
p-Nitrophenyl γ-hydroxypropyl sulphide (BENNETT and BERRY), 1671.
$C_9H_{11}O_3N_3S$ 2-Nitro-4-ethoxyphenylthiocarbamide (DYSON, GEORGE, and HUNTER), 444.
$C_9H_{11}N_2ClS$ *s*-*p*-Chlorophenyldimethylthiocarbamide (HUNTER and STYLES), 1213.
$C_9H_{11}N_2Br_5S$ 1-Dimethylaminobenzthiazole tetrabromide hydrobromide (HUNTER and STYLES), 1211.
$C_9H_{12}ON_2S$ Ethoxyphenylthiocarbamides (DYSON, GEORGE, and HUNTER), 441.
$C_9H_{12}O_2N_2S$ Dimethoxyphenylthiocarbamides (DYSON, GEORGE, and HUNTER), 441.
$C_9H_{12}O_4N_2S$ Nitrobenzylsulphondimethylamides (C. K. and E. H. INGOLD, and SHAW), 826.
Nitrobenzylsulphonethylamides (C. K. and E. H. INGOLD, and SHAW), 825.
$C_9H_{13}O_2NS$ Benzylsulphonethylamide (C. K. and E. H. INGOLD, and SHAW), 818.
$C_9H_{13}O_2N_2Cl$ γ-*p*-Nitrophenylpropylammonium chloride (INGOLD and WILSON), 813.
$C_9H_{14}O_2N_2S$ Ethyl 2-ethylthiolmethylglyoxalinecarboxylate, and its salts (BALABAN and KING), 1866.

9 V

$C_9H_7ON_2ClS$ 5-Chloro-1-acetylaminobenzthiazole (DYSON, HUNTER, and MORRIS), 1190.
$C_9H_{10}O_3NClS$ *p*-Nitrophenyl γ-chloropropyl sulphide (BENNETT and BERRY), 1672.
$C_9H_{10}N_2ClBr_2S$ 5-Chloro-1-dimethylaminobenzthiazole dibromide hydrobromide (HUNTER and STYLES), 1213.
$C_9H_{11}ON_2Br_5S$ 1-Amino-5-ethoxybenzthiazole tetrabromide hydrobromide (DYSON, HUNTER, and MORRIS), 1191.

9 VI

$C_9H_7ON_2ClBr_4S$ 5-Chloro-1-acetamidobenzthiazole tetrabromide (DYSON, HUNTER, and MORRIS), 1191.

C_{10} Group.

$C_{10}H_{16}$ Pinene, recovery of, from its nitroso-chloride (EARL and KENNER), 1269.

10 II

$C_{10}H_8O_2$ 4-Hydroxy-3-methylcoumarin (HEILBRON and HILL), 1706.
4-Methoxycoumarin (HEILBRON and HILL), 1707.
$C_{10}H_8O_4$ 6-Hydroxymethylhomopiperonylolactone (STEVENS), 181.
$C_{10}H_{10}O_2$ Methyl atropate (BAKER and ECCLES), 2129.
Safrole, synthesis of (PERKIN and TRIKOJUS), 1663.
$C_{10}H_{10}O_4$ *m*-Methoxyphenylpyruvic acid (CHAKRAVARTI, HAWORTH, and PERKIN), 2270.
$C_{10}H_{10}N_2$ 2:3-Dimethyl-1:2:3:4-tetrahydroquinoxalines, stereoisomeric, and their tartrates (GIBSON), 342.
$C_{10}H_{12}O_2$ Ethyl phenylacetate, nitration of (BAKER and INGOLD), 834.
$C_{10}H_{12}O_3$ 2:4-Dimethoxymethylbenzaldehydes (ROBERTSON and ROBINSON), 2200.
$C_{10}H_{12}O_5$ Antiarolaldehyde (CHAPMAN, PERKIN, and ROBINSON), 3029.
n-Propyl gallate (CLARKE, ROBINSON, and SMITH), 2649.
Substance, from acetylation of antiarol (CHAPMAN, PERKIN, and ROBINSON), 3033.
Substance, from oxidation of 4:4:5-trimethyl-Δ^5-*cyclo*pentene-1:3-dicarboxylic acid (BHAGVAT and SIMONSEN), 86.
$C_{10}H_{13}Br$ α-Phenylbutyl bromide (EVANS, MABBOTT, and TURNER), 1166.
$C_{10}H_{14}O_2$ Benzyl γ-hydroxypropyl ether (BENNETT and HOCK), 474.
$C_{10}H_{14}O_3$ Camphorquinone, action of sulphuric acid on (BHAGVAT and SIMONSEN), 77.
$C_{10}H_{14}O_4$ αζ-Diacetoxy-$\Delta^{\beta\delta}$-hexadiene (FARMER, LAROIA, SWITZ, and THORPE), 2950.
4-Hydroxy-2:2:3-trimethyl-Δ^3-*cyclo*hexen-5-one-1-carboxylic acid (BHAGVAT and SIMONSEN), 83.
4:4:5-Trimethyl-Δ^5-*cyclo*pentene-1:3-dicarboxylic acids (BHAGVAT and SIMONSEN), 84.
$C_{10}H_{14}O_8$ βγ-Dimethylbutane-$\alpha\alpha\beta\delta$-tetracarboxylic acids (VOGEL), 1990.
$C_{10}H_{16}O$ Pulegones (HUGH, KON, and LINSTEAD), 2585.
$C_{10}H_{16}O_3$ Tetramethyladipic anhydrides (FARMER and KRACOVSKI), 683.
$C_{10}H_{16}O_4$ 4:4:5-Trimethyl*cyclo*pentane-1:3-dicarboxylic acid (BHAGVAT and SIMONSEN), 85.
$C_{10}H_{16}O_5$ 1-Hydroxy-4:4:5-trimethyl*cyclo*pentane-1:3-dicarboxylic acid (BHAGVAT and SIMONSEN), 84.
$C_{10}H_{18}O_2$ 1-Hydroxy-α-ethyl*cyclo*hexaneacetic acid, and its silver salt (KON and NARAYANAN), 1539.
$C_{10}H_{18}O_6$ Tetramethyl gluconolactones (DREW, GOODYEAR, and HAWORTH), 1241; oxidation of (HAWORTH, HIRST, and MILLER), 2436.
Tetramethyl mannonolactone (DREW, GOODYEAR, and HAWORTH), 1243.
$C_{10}H_{18}O_7$ Substance, from oxidation of tetramethyl γ-fructose (HAWORTH, HIRST, and NICHOLSON), 1520.
$C_{10}H_{20}O_3$ β-Hydroxy-β-methyl-α-ethylpentanoic acid, and its silver salt (KON and NARAYANAN), 1544.
$C_{10}H_{20}O_6$ Tetramethylglucose, mutarotation of, in aqueous alcohols (RICHARDS, FAULKNER, and LOWRY), 1733.
Tetramethylglucoses, structure of (HAWORTH, HIRST, and MILLER), 2436.
2:3:4:6-Tetramethylmannose (DREW, GOODYEAR, and HAWORTH), 1243.
$C_{10}H_{21}N$ *d-neoiso*Menthylamine, and its salts (READ and ROBERTSON), 2172.
$C_{10}H_{22}O_2$ αζ-Diethoxyhexane (FARMER, LAROIA, SWITZ, and THORPE), 2951.
$C_{10}H_{24}N_2$ *s*-Tetramethyldiethylethylenediamine, dipicrate of (HANHART and INGOLD), 1011.

10 III

$C_{10}H_6O_2Cl_2$ 1:8-Naphthalyl chloride, preparation and reactions of (DAVIES and LEEPER), 1124.

$C_{10}H_6O_2S$ 1:8-Thionyldihydroxynaphthalene (GREEN), 2344.
$C_{10}H_7O_2N$ Cyanocinnamic acids (DAVIES and POOLE), 2661.
$C_{10}H_7O_2Br_5$ Pentabromosafrole (PERKIN and TRIKOJUS), 1666.
$C_{10}H_7O_4N_3$ 1-Phenyl-4-oximino-5-ketopyrazoline-3-carboxylic acid (CHATTAWAY and HUMPHREY), 2137.
$C_{10}H_8O_3S$ Methyl benzylsulphonate (C. K. and E. H. INGOLD and SHAW), 819.
$C_{10}H_8O_7N_2$ Ethyl 2:4-dinitrobenzoylformate (FAIRBOURNE and FAWSON), 49.
$C_{10}H_9O_2N$ Nitrosodihydro-α-naphthols (ROWE and LEVIN), 531.
$C_{10}H_9O_3N_3$ 1-Phenyl-4-amino-5-ketopyrazoline-3-carboxylic acid, and its hydrochloride (CHATTAWAY and HUMPHREY), 2135.
$C_{10}H_9O_4N$ Methyl *p*-nitroatropate (BAKER and ECCLES), 2131.
Nitrobenzoylacetones (BURGESS), 2018.
6-Nitro*iso*safrole (ROBINSON and ZAKI), 2489.
$C_{10}H_9O_4Br$ 6-Bromomethylhomopiperonylic acid (STEVENS), 186.
$C_{10}H_9O_6N$ *m*-Nitrobenzylmalonic acid (BAKER and ECCLES), 2127.
$C_{10}H_{10}O_{10}Hg$ Mercuretin (MARSH and STRUTHERS), 2658.
$C_{10}H_{11}ON_3$ *cyclo*Pentane*spiro*-2:3-dicyano*cyclo*propane-2-carboxylamide (SIRCAR), 1258.
$C_{10}H_{11}O_2N$ 6-Amino*iso*safrole, and its hydrochloride (ROBINSON and ZAKI), 2490.
5:6-Dimethoxyindole (OXFORD and RAPER), 420.
2:6-Dimethoxy-4-methylbenzonitrile (ROBERTSON and ROBINSON), 2201.
$C_{10}H_{11}O_3N$ Acetopiperonylmethylamide (MALAN and ROBINSON), 2655.
4-Nitro-*ar*-tetrahydro-α-naphthol (ROWE and LEVIN), 531.
$C_{10}H_{11}O_3Cl$ Acetylchlorocreosol (OXFORD), 1966.
$C_{10}H_{11}O_4N$ 6-Hydroxymethylhomopiperonylamide (STEVENS), 182.
$C_{10}H_{11}O_4N_3$ *m*-Nitrobenzylmalonamide (BAKER and ECCLES), 2127.
$C_{10}H_{11}O_6N$ Methyl 3-nitro-2:4-dimethoxybenzoate (DADSWELL and KENNER), 587.
2-Nitro-4:5-dimethoxyphenylacetic acid (OXFORD and RAPER), 419.
$C_{10}H_{12}O_2Se$ Xylyl-4-selenoglycollic acids (PORRITT), 28.
$C_{10}H_{12}O_4N_2$ Acetylnitro-4-methoxytoluidines (DADSWELL and KENNER), 584.
Methyl benzylmethylaminoformate (BAKER), 570.
$C_{10}H_{12}N_2S$ 1-Dimethylaminomethylbenzthiazoles (HUNTER and STYLES), 1212.
$C_{10}H_{12}ON$ Acetoxylidides, and their salts (DADSWELL and KENNER), 1104.
$C_{10}H_{13}OCl$ Benzyl γ-chloropropyl ether (BENNETT and HOCK), 474.
$C_{10}H_{13}O_2N$ Methyl benzylmethylaminoformate (BAKER), 567.
$C_{10}H_{13}O_3N$ 3:5-Dimethoxyacetanilide (OAKESHOTT and PLANT), 489.
2:6-Dimethoxy-4-methylbenzamide (ROBERTSON and ROBINSON), 2200.
$C_{10}H_{13}O_5N$ Oxime from substance $C_{10}H_{12}O_5$ (BHAGVAT and SIMONSEN), 86.
$C_{10}H_{13}N_3S$ Benzaldehyde *S*-ethylthiosemicarbazone, and its hydrochloride (BAIRD, BURNS, and WILSON), 2529.
$C_{10}H_{14}O_2N_2$ Dimethylnitro-β-phenylethylamines, salts of (GOSS, HANHART, and INGOLD), 255.
Nitrobenzyltrimethylamines, picrates of (GOSS, HANHART, and INGOLD), 260.
$C_{10}H_{14}O_3S$ α-Phenylbutanesulphonic acid, sodium salt (EVANS, MABBOTT, and TURNER), 1166.
$C_{10}H_{14}N_2S$ *s*-Tolyldimethylthiocarbamides (HUNTER and STYLES), 1212.
$C_{10}H_{15}ON$ Methoxybenzyldimethylamines, and their hydrochlorides (STEDMAN), 1904.
$C_{10}H_{15}O_2N$ β-2:3-Dimethoxyphenylethylamine, and its salts (HAWORTH), 2283.
*cyclo*Hexanediacetimide (SIRCAR), 604.

$C_{10}H_{11}O_5Cl$ Trihydroxymethoxyflavylium chlorides (ROBERTSON and ROBINSON), 1715.

$C_{10}H_{16}O_4N_6$ 2:2-Dimethyl*cyclo*pentane-3:4-dione-1-carboxylic acid disemicarbazone (GIBSON, HARIHARAN, and SIMONSEN), 3014.

$C_{10}H_{17}ON$ α-Ethyl-Δ^1-*cyclo*hexenylacetamide (KON and NARAYANAN), 1540.

$C_{10}H_{18}O_4S$ Ethyl thiodipropionate (BENNETT and SCORAH), 196.

$C_{10}H_{19}ON_3$ δ-Methyl-γ-ethyl-Δ^δ-hexen-β-one semicarbazone (KON and NARAYANAN), 1545.

$C_{10}H_{19}O_6N$ Substance, from oxidation of tetramethyl γ-fructose (HAWORTH, HIRST, and NICHOLSON), 1521.

$C_{10}H_{20}O_5N_2$ *l*-Arabotrimethoxyglutaromethylamide (HAWORTH and JONES), 2353.
i-Trimethoxyglutaromethylamide (HAWORTH and JONES), 2352.

$C_{10}H_{26}N_2I_2$ *s*-Tetramethyldiethylethylenediammonium di-iodide (HANHART and INGOLD), 1011.

10 IV

$C_{10}H_4O_6N_2Cl_6$ Anhydro-3:5-dinitro-2ββ'β'-trichloro-α-hydroxyethoxy-1-ββ'β'-trichloro-α-hydroxyethylbenzene (CHATTAWAY and MORRIS), 2015.

$C_{10}H_5O_4Cl_7S$ Anhydro-2-ββ'β'-trichloro-α-hydroxyethoxy-1-ββ'β'-trichloro-α-hydroxyethylbenzene-5-sulphonyl chloride (CHATTAWAY and MORRIS), 2016.

$C_{10}H_6ONCl$ *o*-Cyano*allo*cinnamyl chloride (DAVIES and POOLE), 2663.

$C_{10}H_6O_5Cl_6S$ Anhydro-2-ββ'β'-trichloro-α-hydroxyethoxy-1-ββ'β'-trichloro-α-hydroxyethylbenzene-5-sulphonic acid, and its ammonium salt (CHATTAWAY and MORRIS), 2014.

$C_{10}H_8O_2NCl$ 6-Chloromethylhomopiperonylonitrile (STEVENS), 182.

$C_{10}H_6O_6N_2Cl_2$ ωω-Dichloro-3:5-dinitro-2-ethoxyacetophenone (CHATTAWAY and MORRIS), 2016.

$C_{10}H_9O_2NS$ Carbethoxyphenylthiocarbimides (DYSON, GEORGE, and HUNTER), 441.

$C_{10}H_9O_3NS$ 3-Keto-2:3-dihydro-1:4-benzthiazine-2-acetic acid (MILLS and WHITWORTH), 2751.

$C_{10}H_{10}O_2N_2Cl_2$ Ethyl glyoxylate 2:4-dichlorophenylhydrazone (CHATTAWAY and BENNETT), 2851.

$C_{10}H_{10}O_2N_2Br_2$ Ethyl glyoxylate 2:4-dibromophenylhydrazone (CHATTAWAY and BENNETT), 2852.

$C_{10}H_{10}O_2N_2S$ 1-Amino-5-carbethoxybenzthiazole (DYSON, HUNTER, and MORRIS), 1190.

$C_{10}H_{10}O_3NCl$ Ethyl β-4-hydroxypiperidylacetate methochloride (MILLS, PARKIN, and WARD), 2624.

$C_{10}H_{11}ONS$ 4-Keto-2-methyltetrahydro-1:5-heptabenzthiazine (MILLS and WHITWORTH), 2749.

$C_{10}H_{12}ONCl$ Chloroaceto-*m*-2-xylidides (DADSWELL and KENNER), 1106.

$C_{10}H_{12}ONI$ 1-Methylbenzoxazole ethiodide (HAMER), 2803.

$C_{10}H_{12}ON_2S$ 1-Dimethylamino-5-methoxybenzthiazole (HUNTER and STYLES), 1212.

$C_{10}H_{12}O_2NBr$ Methylbromopiperonylethylamine, and its salts (STEVENS), 185.

$C_{10}H_{12}O_2N_2S$ Carbethoxyphenylthiocarbamides (DYSON, GEORGE, and HUNTER), 441.

$C_{10}H_{12}N_2Br_4S$ 1-Dimethylamino-3-methylbenzthiazole tetrabromide (HUNTER and STYLES), 1212.

$C_{10}H_{12}N_2Br_6S$ 1-Dimethylamino-5-methylbenzthiazole hexabromide (HUNTER and STYLES), 1213.

$C_{10}H_{13}N_2Br_5S$ 1-Dimethylamino-5-methylbenzthiazole tetrabromide hydrobromide (HUNTER and STYLES), 1212.

$C_{10}H_{14}ON_2S$ *s*-*p*-Methoxyphenyldimethylthiocarbamide (HUNTER and STYLES), 1212.

$C_{10}H_{15}O_2N_2I$ *p*-Nitrobenzyltrimethylammonium iodide (STEDMAN), 1905.

$C_{10}H_{15}O_5N_2As$ 3-Nitro-6-diethylaminophenylarsinic acid (BURTON and GIBSON), 2388.

$C_{10}H_{20}O_2NBr$ Ethyl 4-hydroxy-1-piperidylacetate methobromides (MILLS, PARKIN, and WARD), 2622.

10 V

$C_{10}H_5O_4NCl_6S$ Anhydro-2-$\beta\beta\beta$-trichloro-α-hydroxyethoxy-1-$\delta\beta\beta$-trichloro-α-hydroxyethylbenzene-5-sulphondichloroamide (CHATTAWAY and MORRIS), 2017.

$C_{10}H_7O_4NCl_6S$ Anhydro-2-$\delta\beta\delta$-trichloro-α-hydroxyethoxy-1-$\beta\beta\beta$-trichloro-α-hydroxyethylbenzene-5-sulphonamide (CHATTAWAY and MORRIS), 2017.

$C_{10}H_{10}O_2N_2ClBr$ Ethyl glyoxylate chlorobromophenylhydrazones (CHATTAWAY and BENNETT), 2852.

$C_{10}H_{10}O_2N_2Br_2S$ 1-Amino-5-carbethoxybenzthiazole dibromide (DYSON, HUNTER, and MORRIS), 1190.

$C_{10}H_{12}ON_2Cl_5Mo$ Dipyridinium molybdenyl pentachloride (JAMES and WARDLAW), 2148.

$C_{10}H_{12}ON_2Br_4S$ 1-Dimethylamino-5-methoxybenzthiazole tetrabromide (HUNTER and STYLES), 1212.

$C_{10}H_{13}O_2N_2Cl_7As$ 3-Nitro-6-diethylaminophenylarsenious chloride (BURTON and GIBSON), 2388.

C_{11} Group.

$C_{11}H_9Br_3$ 5-Bromo-α-naphthylmethyl bromide (SHOESMITH and RUBLI), 3104.

$C_{11}H_{10}O_3$ 4-Methoxy-3-methylcoumarin (HEILBRON and HILL), 1707.

$C_{11}H_{10}O_5$ 3:4-Dimethoxyhomophthalic anhydride (HAWORTH, KOEPFLI, and PERKIN), 551.

$C_{11}H_{10}O_6$ *O*-Diacetylphloroglucinaldehyde (ROBERTSON and ROBINSON), 1712.

$C_{11}H_{12}O_5$ 6-Methoxymethylhomopiperonylic acid, and its silver salt (STEVENS), 185.

5-Methylcarbonato-orcylaldehyde 3-methyl ether (HIRST), 2495.

$C_{11}H_{13}N_3$ 8-Amino-2:4-dimethylquinoline (ROBERTS and TURNER), 1856.

$C_{11}H_{14}O_3$ Ethyl *m*-tolyloxyacetate (SMITH), 176.

Propylvanillins (DICKINSON, HEILBRON, and IRVING), 1895.

$C_{11}H_{14}O_5$ *O*-Acetylantiarol (CHAPMAN, PERKIN, and ROBINSON), 3029.

$C_{11}H_{14}O_6$ ω-5:6-Trimethoxyresacetophenone (CHAPMAN, PERKIN, and ROBINSON) 3033.

$C_{11}H_{16}O_2$ Benzyl δ-hydroxybutyl ether (BENNETT and HOCK), 475.

4-*n*-Butoxyanisole (CLARKE, ROBINSON, and SMITH), 2651.

$C_{11}H_{16}O_4$ Methyl 4-hydroxy-2:2:3-trimethyl-Δ^3-cyclohexen-5-one-1-carboxylate (BHAGVAT and SIMONSEN), 82.

$C_{11}H_{16}O_6$ Acetyl-α-keto-$\beta\beta\gamma\gamma$-tetramethylglutaric hydroxylactone (ROTHSTEIN and SHOPPEE), 534.

$C_{11}H_{18}O_2$ $\beta\beta$-Di*iso*butylacrylic acid (KON and MAY), 1554.

$C_{11}H_{18}O_4$ α-Ethyl*cyclo*pentane-1:1-diacetic acid, and its silver salt (KON and NARAYANAN), 1544.

$C_{11}H_{18}O_6$ Dimethyl γ-mannonolactone-acetone (GOODYEAR and HAWORTH), 3142.

$C_{11}H_{20}O_2$ Ethyl-1-hydroxy-α-ethyl*cyclo*pentaneacetate (KON and NARAYANAN), 1543.

$C_{11}H_{20}O_7$ Substance, from oxidation of tetramethylfructose (HAWORTH, HIRST, and LEARNER), 1047; (AVERY, HAWORTH, and HIRST), 2313.

11 III

$C_{11}H_5O_3Cl_7$ Acid chloride of anhydro-5-carboxy-2-$\beta\beta\beta$-trichloro-α-hydroxyethoxy-1-$\beta\beta\beta$-trichloro-α-hydroxyethylbenzene (CHATTAWAY and PRATS), 689.

$C_{11}H_6O_4Cl_6$ Anhydro-5-carboxy-2-$\beta\beta\beta$-trichloro-α-hydroxyethoxy-1-$\beta\beta\beta$-trichloro-α-hydroxyethylbenzene (CHATTAWAY and PRATS), 687.

$C_{11}H_7NCl_4$ Tetrachloro-2:4-dimethylquinolines (ROBERTS and TURNER), 1848.

$C_{11}H_8O_4N_2$ Anhydrodiketosuccinic acid tolylhydrazones (CHATTAWAY and HUMPHREY), 2794.

$C_{11}H_8O_8N_4$ Ethyl 2:4:6-trinitrophenylcyanoacetate (FAIRBOURNE and FAWSON) 48.

$C_{11}H_8NCl_3$ Trichloro-2:4-dimethylquinolines (ROBERTS and TURNER), 1852.

$C_{11}H_9OBr$ 5-Bromo-α-naphthylcarbinol (SHOESMITH and RUBLI), 3104.

4-Bromo-α-naphthyl methyl ether (SHOESMITH and RUBLI), 3102.

$C_{11}H_9O_5Br$ 6-Bromo-3:4-dimethoxyhomophthalic anhydride (HAWORTH, KOEPFLI, and PERKIN), 551.

$C_{11}H_9O_6N_3$ Ethyl 2:4-dinitrophenylcyanoacetate, and its sodium salt (FAIRBOURNE and FAWSON), 47.

$C_{11}H_9NCl_2$ Dichloro-2:4-dimethylquinolines (ROBERTS and TURNER), 1846.

$C_{11}H_{10}ON_2$ 3-Keto-3:4:5:6-tetrahydro-4-carboline (MANSKE and ROBINSON), 242.

$C_{11}H_{10}O_2N_2$ 8-Nitro-2:4-dimethylquinoline (ROBERTS and TURNER), 1856.

$C_{11}H_{10}O_5N_2$ Diketosuccinic acid tolylhydrazones (CHATTAWAY and HUMPHREY), 2794.

$C_{11}H_{10}NCl$ Chloro-2:4-dimethylquinolines (ROBERTS and TURNER), 1845.

$C_{11}H_{10}NBr$ 4-Bromo-2-methyl-α-naphthylamine (SHOESMITH and RUBLI), 3103.

$C_{11}H_{10}N_2Cl_2$ Dichloroamino-2:4-dimethylquinolines (ROBERTS and TURNER), 1850.

$C_{11}H_{11}O_3Br$ 4-Bromo-6:7-dimethoxy-1-hydrindone (HAWORTH, KOEPFLI, and PERKIN), 550.

$C_{11}H_{11}O_4N$ 5:6-Dimethoxyindole-2-carboxylic acid (OXFORD and ROPER), 420.

$C_{11}H_{11}O_4Cl_3$ 5-Carboxy-2-ethoxy-1-$\beta\beta\beta$-trichloro-α-hydroxyethylbenzene (CHATTAWAY and PRATS), 689.

$C_{11}H_{11}O_4Br$ Methyl 6-bromomethylhomopiperonylate (STEVENS), 186.

$C_{11}H_{11}O_5Br$ 6-Bromo-3:4-dimethoxyhomophthalic acid (HAWORTH, KOEPFLI, and PERKIN), 551.

$C_{11}H_{11}N_2Cl$ Chloroamino-2:4-dimethylquinolines (ROBERTS and TURNER), 1848.

$C_{11}H_{13}ON$ γ-Benzyloxybutyronitrile (BENNETT and HOCK), 474.

$C_{11}H_{13}ON_3$ β-3-Indolylpropionhydrazide (MANSKE and ROBINSON), 241.

$C_{11}H_{13}O_4Br$ β-6-Bromoveratrylpropionic acid (HAWORTH, KOEPFLI, and PERKIN), 550.

$C_{11}H_{13}N_3S$ Benzaldehyde *S*-allylthiosemicarbazone, and its hydrochloride (BAIRD, BURNS, and WILSON), 2530.

$C_{11}H_{15}ON_3$ *meso*-1-Carbamyl-2:3-dimethyl-1:2:3:4-tetrahydroquinoxaline (GIBSON), 345.

$C_{11}H_{15}OCl$ Benzyl chlorobutyl ether (BENNETT and HOCK), 476.

$C_{11}H_{15}O_3N$ β-2:3-Dimethoxyphenylpropionamide (HAWORTH), 2282.

$C_{11}H_{15}O_4N$ Nitro-4-*n*-butoxyanisole (CLARKE, ROBINSON, and SMITH), 2649.

$C_{11}H_{16}O_5N_2$ Antiarolaldehyde semicarbazone (CHAPMAN, PERKIN, and ROBINSON), 3030.

Semicarbazone from substance $C_{10}H_{12}O_5$ (BHAGVAT and SIMONSEN), 86.

$C_{11}H_{15}N_3S$ Acetone δ-benzylthiosemicarbazone (BAIRD, BURNS, and WILSON), 2530.

Benzaldehyde *S*-propylthiosemicarbazone, and its hydrochloride (BAIRD, BURNS, and WILSON), 2529.

$C_{11}H_{16}ON_4$ Methyl ethyl ketone δ-anilinosemicarbazone (BAIRD and WILSON), 2115.

$C_{11}H_{16}O_3N_2$ Trimethylnitro-β-phenylethylamines, salts of (GOSS, HANHART, and INGOLD), 257.

$C_{11}H_{16}O_3Br$ Methyl 5:5-dibromo-2:2:3-trimethyl*cyclo*hexan-4-one-1-carboxylate (BHAGVAT and SIMONSEN), 82.

$C_{11}H_{17}ON$ Methylephedrines, and their salts (SMITH), 2057.

$C_{11}H_{17}O_4N$ Methyl 5-oximino-2:2:3-trimethyl*cyclo*hexan-4-one-1-carboxylate (BHAGVAT and SIMONSEN), 87.

$C_{11}H_{18}O_4N_2$ Methyl 4-hydroxy-2:2:3-trimethyl-Δ^3-*cyclo*hexen-ζ-one-1-carboxylate dioxime (BHAGVAT and SIMONSEN), 82.

$C_{11}H_{21}ON_3$ δ-*d*-Bornylsemicarbazides, and their hydrochlorides (GOODSON), 1998.

$C_{11}H_{22}O_2N_2$ *n*-Nonanedicarboxyamide (BARNICOAT), 2928.

$C_{11}H_{23}N_3S$ Acetone δ-heptylthiosemicarbazone (BAIRD, BURNS, and WILSON), 2533.

11 IV

$C_{11}H_8O_2NCl_6$ Anhydro-5-cyano-2-$\beta\beta\beta$-trichloro-α-hydroxyethoxy-1-$\beta\beta\beta$-trichloro α-hydroxyethylbenzene (CHATTAWAY and PRATS), 688.

$C_{11}H_7O_3NCl_6$ Amide of anhydro-5-carboxy-2-$\beta\beta\beta$-trichloro-α-hydroxyethoxy-1-$\beta\beta\beta$-trichloro-α-hydroxyethylbenzene (CHATTAWAY and PRATS), 689.

$C_{11}H_7O_6NS_2$ *ON*-Carbonyl-1:8-aminonaphthol-3:6-disulphonic acid, salts (BALABAN and KING), 3091.

$C_{11}H_8O_2N_2Cl_2$ Dichloronitro-2:4-dimethylquinoline (ROBERTS and TURNER), 1847.

$C_{11}H_8O_5Cl_6S$ Methyl anhydro-2-$\beta\beta\beta$-trichloro-α-hydroxyethyl-1-$\beta\beta\beta$-trichloro-α-hydroxyethylbenzene-5-sulphonate (CHATTAWAY and MORRIS), 2017.

$C_{11}H_8O_6N_2Cl$ Ethyl 2:4-dinitrochlorophenylcyanoacetate (FAIRBOURNE and FAWSON), 50.

$C_{11}H_8O_6N_2Br$ Ethyl 2:4-dinitrobromophenylcyanoacetate (FAIRBOURNE and FAWSON), 49.

$C_{11}H_8O_7N_2Br$ Ethyl-2:4-dinitrobromophenylhydroxycyanoacetate (FAIRBOURNE and FAWSON), 50.

$C_{11}H_9O_2N_2Cl$ Chloronitro-2:4-dimethylquinolines (ROBERTS and TURNER), 1848.

$C_{11}H_{10}O_2NCl$ γ-Chloro-α-cyanopropyl benzoate (CRAWFORD and KENYON), 400.

$C_{11}H_{10}O_4NBr$ 6-Bromo-2-carboxy-3:4-dimethoxyphenylacetonitrile (HAWORTH, KOEPFLI, and PERKIN), 551.

4-Bromo-2-*iso*nitroso-6:7-dimethoxy-1-hydrindone (HAWORTH, KOEPFLI, and PERKIN), 550.

$C_{11}H_{11}ONCl_2$ β-Dichloroanilinopropenyl methyl ketones (ROBERTS and TURNER), 1843.

$C_{11}H_{11}O_2NS$ Acetyl-4-ketotetrahydro-1:5-heptabenzthiazine (MILLS and WHITWORTH), 2750.

$C_{11}H_{11}O_3NS$ 4-Ketotetrahydro-1:5-heptabenzthiazine-2-acetic acids, and their salts (MILLS and WHITWORTH), 2743.

$C_{11}H_{11}O_4N_3Br_2$ 1:3-Dibromo-2:4-dinitro-5-piperidinobenzene (LE FÈVRE and TURNER), 1119.

$C_{11}H_{12}ONCl$ β-Chloroanilinopropenyl methyl ketones (ROBERTS and TURNER), 1842.

$C_{11}H_{12}O_2N_2Cl_2$ 4:5-Dichloro-1-nitro-2-piperidinobenzene (LE FÈVRE and TURNER), 1117.

n-Propyl glyoxylate 2:4-dichlorophenylhydrazone (CHATTAWAY and BENNETT), 2851.

$C_{11}H_{12}O_3N_2Br_2$ *n*-Propyl glyoxylate 2:4-dibromophenylhydrazone (CHATTAWAY and BENNETT), 2852.

$C_{11}H_{12}O_3NBr$ 4-Bromo-6:7-dimethoxy-1-hydrindone oxime (HAWORTH, KOEPFLI, and PERKIN), 550.

$C_{11}H_{12}O_4N_4S$ Penthian-4-one 2:4-dinitrophenylhydrazone (BENNETT and SCORAH), 199.

$C_{11}H_{12}NBrS$ 1-Methylbenzthiazole allobromide (HAMER), 2802.
$C_{11}H_{13}O_3NS$ *o*-Diacetylaminothioanisole (MILLS and WHITWORTH), 2752.
$C_{11}H_{13}O_3N_3Cl$ 2-Chloro-4-nitropiperidinobenzene (LE FÈVRE and TURNER), 1117.
$C_{11}H_{13}O_3N_2Br$ 4-Bromo-2-nitropiperidinobenzene (LE FÈVRE and TURNER), 1117.
$C_{11}H_{14}ON_2S$ 1-Dimethylamino-5-ethoxybenzthiazole (HUNTER and STYLES), 1212.
$C_{11}H_{15}O_2N_3S$ *S-o*-Carbethoxybenzylthiosemicarbazide, dihydrochloride of (BAIRD, BURNS, and WILSON), 2530.
$C_{11}H_{15}O_5N_2As$ 3-Nitro-4-piperidinophenylarsinic acid, and its salts (KING), 1053.
$C_{11}H_{16}ON_2S$ *s-p*-Ethoxyphenyldimethylthiocarbamide (HUNTER and STYLES), 1212.
$C_{11}H_{18}O_2NI$ Piperonylmethyltrimethylammonium iodide (MALAN and ROBINSON), 2655.
$C_{11}H_{17}O_2NS$ Benzylsulphondiethylamide (C. K. and E. H. INGOLD and SHAW), 819.
$C_{11}H_{17}O_3N_2As$ 3-Amino-4-piperidinophenylarsinic acid, and its salts (KING), 1053.

11 V

$C_{11}H_{14}ON_2Br_4S$ 1-Dimethylamino-5-ethoxybenzthiazole tetrabromide (HUNTER and STYLES), 1212.

C_{12} Group.

12 II

$C_{12}H_{20}$ 6ε-Dimethyl-aζ-diethylhexatriene (FARMER, LAROIA, SWITZ, and THORPE), 2958.
$C_{12}H_7Br_3$ 2:4:6-Tribromodiphenyl (BLAKEY and SCARBOROUGH), 3008.
$C_{12}H_8Cl_2$ 2:5-Dichlorodiphenyl (SCARBOROUGH and WATERS), 94.
$C_{12}H_8Br_2$ 2:5-Dibromodiphenyl (SCARBOROUGH and WATERS), 94.
Dibromodiphenyls (BLAKEY and SCARBOROUGH), 3007.
$C_{12}H_{10}O_2$ 3-Methoxy-α-naphthaldehyde (SHOESMITH and RUBLI), 3101.
$C_{12}H_{10}N_2$ Harman (MANSKE, PERKIN, and ROBINSON), 11.
$C_{12}H_{11}Br$ 4-Methyl-α-naphthylmethyl bromide (SHOESMITH and RUBLI), 3102.
$C_{12}H_{12}O_2$ Methoxy-α-naphthylcarbinols (SHOESMITH and RUBLI), 3102.
$C_{12}H_{12}N_2$ Harmalan (MANSKE, PERKIN, and ROBINSON), 11.
$C_{12}H_{14}O_5$ Ethyl 2-hydroxy-1:5-*iso*phthalate (CHATTAWAY and PRATS), 690.
Methyl 6-methoxymethylhomopiperonylate (STEVENS), 185.
$C_{12}H_{14}O_6$ 4:5-Dimethoxy-2:6-diacetylresorcinol (CHAPMAN, PERKIN, and ROBINSON), 3033.
$C_{12}H_{15}N$ *trans*-Hexahydrocarbazole, and its picrate (GURNEY, PERKIN, and PLANT), 2676.
$C_{12}H_{15}N_3$ 5-Keto-6-methyl-2:3:4:5-tetrahydropyridine 5-phenylhydrazone, and its hydrochloride (MANSKE, PERKIN, and ROBINSON), 9.
$C_{12}H_{16}O_4$ Ethyl β-*m*-methoxyphenoxypropionate (PERKIN, RÂY, and ROBINSON), 2097.
Ethyl phenylmalonate, nitration of (BAKER and INGOLD), 835.
$C_{12}H_{16}O_5$ 4-Acetoxy-2:2:3-trimethyl-Δ^3-*cyclo*hexen-5-one-1-carboxylic acid (BHAGVAT and SIMONSEN), 83.
$C_{12}H_{16}N_2$ Aminohexahydrocarbazoles (GURNEY and PLANT), 1317.
$C_{12}H_{17}N$ 4-Phenyl-1-methylpiperidine, and its salts (MILLS, PARKIN, and WARD), 2618.
$C_{12}H_{18}O_2$ β-Thujylideneacetic acid (HUGH and KON), 2597.
Acid, and its silver salt, from dehydration of ethyl thujolacetate (HUGH and KON), 2598.

$C_{12}H_{18}O_3$ 4-Methyl-5-*cyclo*hexane*spirocyclo*pentan-3-one-1-carboxylic acid (INGOLD and SEELEY), 1689.

$C_{12}H_{18}O_4$ *l*-4-Acetyl-2:2:3-trimethyl-Δ^3-*cyclo*hexene-1-carboxylic acid (BHAGVAT, SIMONSEN, and RAO), 88.

$C_{12}H_{18}O_6$ 1-Acetoxy-4:4:5-trimethyl*cyclo*pentane-1:3-dicarboxylic acid (BHAGVAT and SIMONSEN), 84.

γ-Mannonolactone-diacetone (GOODYEAR and HAWORTH), 3143.

$C_{12}H_{19}N$ β-Phenylethyldimethylethylamine, picrate of (HANHART and INGOLD), 1008.

$C_{12}H_{20}O_4$ Ethyl 2:3-dimethyl*cyclo*butane-1:4-dicarboxylate (VOGEL), 1992.

$C_{12}H_{20}N$ γ-Phenylpropyltrimethylamine, picrate of (INGOLD and WILSON), 810.

$C_{12}H_{20}Br_2$ εζ-Dibromo-δη-dimethyl-Δγη-decadiene (FARMER, LAROIA, SWITZ, and THORPE), 2957.

$C_{12}H_{22}O_2$ 5-Acetyl-1:3:3:4:4-pentamethyl*cyclo*pentan-1-ol (VOGEL), 598.

δη-Dimethyl-Δγη-decadiene-εζ-diol (FARMER, LAROIA, SWITZ, and THORPE), 2957.

$C_{12}H_{22}O_4$ Ethyl ββ′-dimethyladipate (VOGEL), 1991.

Ethyl hydrogen *iso*heptylmalonate (KON and MAR), 1554.

$C_{12}H_{22}O_{11}$ Cellobiose, constitution of (HAWORTH, LONG, and PLANT), 2809.

Lactose, constitution of (HAWORTH and LONG), 544.

Maltose, constitution of (HAWORTH, LOACH, and LONG), 3146.

Melibiose, constitution of (CHARLTON, HAWORTH, and HICKINBOTTOM), 1527; (HAWORTH, LOACH, and LONG), 3146.

Sucrose, constitution of (HAWORTH, HIRST, and NICHOLSON), 1513; (AVERY, HAWORTH, and HIRST), 2308; vapour pressures of mixtures of methyl acetate, water, and (MCKEOWN and STOWELL), 97.

Turanose (LEITCH), 588.

$C_{12}H_{24}N_2$ Pinacolinazine (BAIRD and WILSON), 2116.

12 III

$C_{12}H_6O_8N_4$ Tetranitrodiphenyl (BLAKEY and SCARBOROUGH), 3006.

$C_{12}H_6Cl_4S_2$ 2:5-Dichlorophenyl trisulphide (BROOKER, CHILD, and SMILES), 1387.

$C_{12}H_6Br_4S_2$ 2:5-Dibromophenyl trisulphide (BROOKER, CHILD, and SMILES), 1387.

$C_{12}H_7OBr_3$ 3:5:4′-Tribromo-4-hydroxydiphenyl (BELL and ROBINSON), 1131.

$C_{12}H_7O_2N$ 1-Cyano-8-naphthoic acid (DAVIES and LEEPER), 1126.

$C_{12}H_7NBr_4$ Tetrabromo-3-aminodiphenyl (BLAKEY and SCARBOROUGH), 3005.

$C_{12}H_8OBr_2$ 3:4′-Dibromo-4-hydroxydiphenyl (BELL and ROBINSON), 1131.

$C_{12}H_8O_6N_4$ 2′:3:4′-Trinitro-4-aminodiphenyl (LE FÈVRE, MOIR, and TURNER), 2337.

$C_{12}H_8NCl_3$ 2′:4:4′-Trichloro-3-aminodiphenyl (BLAKEY and SCARBOROUGH), 3004.

$C_{12}H_8NBr_3$ 2:4:6-Tribromo-3-aminodiphenyl (BLAKEY and SCARBOROUGH), 3008.

$C_{12}H_9OBr$ Bromo-4-hydroxydiphenyls (BELL and ROBINSON), 1131.

$C_{12}H_9O_2Cl$ 3-Methoxy-α-naphthoyl chloride (SHOESMITH and RUBLI), 3101.

$C_{12}H_9O_4N_3$ Dinitro-2-aminodiphenyl (SCARBOROUGH and WATERS), 96.

$C_{12}H_9O_6N_5$ 2:3:5′-Trinitrobenzidine (LE FÈVRE, MOIR, and TURNER), 2338.

$C_{12}H_9NCl_2$ 3:5-Dichloro-2-aminodiphenyl, and its hydrochloride (SCARBOROUGH and WATERS), 92.

$C_{12}H_9NBr_2$ 3:5-Dibromo-2-aminodiphenyl (SCARBOROUGH and WATERS), 95.

$C_{12}H_{10}O_3N_2$ 4′-Nitro-2-aminodiphenyl (SCARBOROUGH and WATERS), 96.

Nitro-3-aminodiphenyls (BLAKEY and SCARBOROUGH), 3008.

γ-Phthalimidobutyronitrile, preparation of (MANSKE, PERKIN, and ROBINSON), 6.

$C_{12}H_{10}NCl$ Chloro-3-aminodiphenyls (BLAKEY and SCARBOROUGH), 3008.

$C_{12}H_{10}NBr$ 5-Bromo-2-aminodiphenyl, and its hydrochloride (Scarborough and Waters), 94.

Bromo-3-aminodiphenyls (Blakey and Scarborough), 3005.

$C_{12}H_{10}Cl_2Si$ Diphenylsilicon dichloride, preparation of (Kipping and Murray), 2734.

$C_{12}H_{11}OBr$ Methoxy-α-naphthylmethyl bromides (Shoesmith and Rubli), 3101.

$C_{12}H_{11}O_2N$ Methoxy-1-naphthaldoximes (Brady and Goldstein), 1962.

$C_{12}H_{11}O_4N$ Methyl 3-hydroxyindole-2-carboxylate (Robertson), 1939.

$C_{12}H_{11}O_4N_3$ 1-Phenyl-4-acetylamino-5-ketopyrazoline-3-carboxylic acid (Chattaway and Humphrey), 2136.

$C_{12}H_{11}O_6N$ Methyl nitrobenzylidenemalonates (Baker and Eccles), 2126.

$C_{12}H_{13}O_2N$ Methyl β-3-indolylpropionate (Manske and Robinson), 241.

$C_{12}H_{13}O_2N_3$ 1-Nitroanilino-1-cyano*cyclo*pentanes (Oakeshott and Plant), 491.

$C_{12}H_{13}O_3N$ 1-Acetyl-5:6-dimethoxyindole (Oxford and Raper), 421.

$C_{12}H_{13}O_6N$ Methyl nitrobenzylmalonates (Baker and Eccles), 2127.

$C_{12}H_{14}O_2N_2$ Nitrohexahydrocarbazoles (Gurney and Plant), 1317.

$C_{12}H_{14}O_4N_2$ 1-Nitroanilino*cyclo*pentane-1-carboxylic acids (Oakeshott and Plant), 492.

$C_{12}H_{14}NBr$ 6-Bromohexahydrocarbazole, and its hydrobromide (Gurney and Plant), 1321.

$C_{12}H_{14}N_2Cl$ 5-Keto-6-methyl-2:3:4:5-tetrahydropyridine 5-*m*-chlorophenylhydrazone, and its hydrochloride (Manske, Perkin, and Robinson), 10.

$C_{12}H_{15}O_3N_3$ 1-Nitroanilino*cyclo*pentane-1-carboxyamides (Oakeshott and Plant), 491.

$C_{12}H_{16}O_4N_2$ 8-Nitro-5:6-dimethoxy-2-methyl-1:2:3:4-tetrahydro*iso*quinoline (Haworth), 2284.

$C_{12}H_{17}O_2N$ 5:6-Dimethoxy-2-methyl-1:2:3:4-tetrahydro*iso*quinoline, and its salts (Haworth), 2283.

$C_{12}H_{17}O_3N_3$ Propylvanillin semicarbazones (Dickinson, Heilbron, and Irving), 1895.

$C_{12}H_{17}O_4N$ Methyl ethyl β-cyano-Δ$^{\delta}$-hexene-βζ-dicarboxylate (Farmer and Healey), 1065.

$C_{12}H_{17}N_3S$ Acetone δ-α-phenylethylthiosemicarbazone (Baird, Burns, and Wilson), 2532.

Benzaldehyde *S*-butylthiosemicarbazone (Baird, Burns, and Wilson), 2530.

$C_{12}H_{19}O_3N_3$ Nitrophenylpropyltrimethylamines, picrates of (Ingold and Wilson), 811.

$C_{12}H_{20}NI$ β-Phenylethyldimethylethylammonium iodide (Hanhart and Ingold), 1007.

$C_{12}H_{24}O_2N_2$ *n*-Decanedicarboxyamide (Barnicoat), 2928.

12 IV

$C_{12}H_3ONCl_6$ Hexachlorobenzoquinoneanil (Bradfield, Cooper, and Orton), 2858.

$C_{12}H_4ONCl_5$ 2:6:2′:4′:6′-Pentachlorobenzoquinoneanil (Bradfield, Cooper, and Orton), 2858.

$C_{12}H_4ONCl_7$ Heptachloro-4-hydroxydiphenylamine (Bradfield, Cooper, and Orton), 2859.

$C_{12}H_4ONBr_5$ Pentabromobenzoquinoneanil (Bradfield, Cooper, and Orton), 2861.

$C_{12}H_5ONCl_4$ 2:6:2′:4′-Tetrachlorobenzoquinoneanil (Bradfield, Cooper, and Orton), 2857.

$C_{12}H_5ONCl_6$ Hexachlorohydroxydiphenylamine (Bradfield, Cooper, and Orton), 2858.

$C_{12}H_5O_2NCl_4$ Tetrachloro-3-nitrodiphenyl (BLAKEY and SCARBOROUGH), 3004.
$C_{12}H_6ONCl_3$ 2:2′:4′-Trichlorobenzoquinoneanil (BRADFIELD, COOPER, and ORTON), 2857.
$C_{12}H_6ONCl_5$ 2:6:2′:4′:6′-Pentachloro-4-hydroxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2858.
$C_{12}H_6ONBr_5$ Pentabromo-4-hydroxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2861.
$C_{12}H_6O_2NCl_3$ Trichloro-3-nitrodiphenyl (BLAKEY and SCARBOROUGH), 3004.
$C_{12}H_6O_5N_2Cl_2$ Dinitro-4:4′-dichlorodiphenyl ether (LE FÈVRE, SAUNDERS, and TURNER), 1172.
$C_{12}H_6O_5N_2Br_2$ Dibromodinitrodiphenyl ethers (LE FÈVRE, SAUNDERS, and TURNER), 1171.
$C_{12}H_6O_5N_2Te$ Dinitrophenoxtellurines (DREW and THOMASON), 122.
$C_{12}H_7ONCl_2$ 2′:4′-Dichloro-3-nitrodiphenyl (BLAKEY and SCARBOROUGH), 3004.
$C_{12}H_7O_3NBr_2$ 3:4′-Dibromo-5-nitro-4-hydroxydiphenyl (BELL and ROBINSON), 1131.
Nitro-4:4′-dibromodiphenyl ether (LE FÈVRE, SAUNDERS, and TURNER), 1172.
$C_{12}H_7O_3NTe$ Nitrophenoxtellurines (DREW and THOMASON), 121.
$C_{12}H_7O_4N_2Br$ 4-Bromo-3:4′-dinitrodiphenyl (LE FÈVRE, MOIR, and TURNER), 2336.
$C_{12}H_7O_5N_2Br$ 5-Bromo-3:4′-dinitro-4-hydroxydiphenyl (BELL and ROBINSON), 1133.
$C_{12}H_8ONCl$ 4′-Chlorobenzoquinoneanil (BRADFIELD, COOPER, and ORTON), 2856.
$C_{12}H_8ONCl_3$ 2:2′:4′-Trichloro-4-hydroxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2857.
$O_{12}H_8ONBr$ 4′-Bromobenzoquinoneanil (BRADFIELD, COOPER, and ORTON), 2860.
$C_{12}H_8O_2NCl$ 4′-Chloro-3-nitrodiphenyl (BLAKEY and SCARBOROUGH), 3003.
$C_{12}H_8O_2NBr$ 4′-Bromo-3-nitrodiphenyl (BLAKEY and SCARBOROUGH), 3004.
Bromonitrodiphenyls (SCARBOROUGH and WATERS), 96, 1138.
$C_{12}H_8O_2N_2Br_2$ 5:4′-Dibromo-3-nitro-4-aminodiphenyl (SCARBOROUGH and WATERS), 1138.
$C_{12}H_8O_3NBr$ 4-Bromo-4′-nitrodiphenyl ether (LE FÈVRE, SAUNDERS, and TURNER), 1171.
Bromonitro-4-hydroxydiphenyls (BELL and ROBINSON), 1132.
$C_{12}H_9ONTe$ 2-Aminophenoxtellurine (DREW and THOMASON), 124.
$C_{12}H_9O_3N_2Cl$ 4′-Chloro-3-nitro-4-aminodiphenyl (SCARBOROUGH and WATERS), 1138.
$C_{12}H_9O_3N_2Br$ 4-Bromo-4′-nitro-3-aminodiphenyl (BLAKEY and SCARBOROUGH), 3009.
Bromonitro-4-aminodiphenyls (SCARBOROUGH and WATERS), 1138.
$C_{12}H_9O_4N_2As$ Nitrophenarsaziuic acid (GIBSON and JOHNSON), 2514.
$C_{12}H_{10}ONCl$ 4-Chloro-4′-aminodiphenyl ether (LE FÈVRE, SAUNDERS, and TURNER), 1172.
4′-Chloro-4-hydroxydiphenylamine, and its toluenesulphonate (BRADFIELD, COOPER, and ORTON), 2856.
$C_{12}H_{10}ONBr$ 4′-Bromo-4-hydroxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2860.
$C_{12}H_{10}ON_2Te$ Diaminophenoxtellurines (DREW and THOMASON), 124.
$C_{12}H_{10}O_5Cl_6S$ Ethyl anhydro-2-$\beta\beta\beta$-trichloro-α-hydroxyethoxy-1-$\beta\beta\beta$-trichloro-α-hydroxyethylbenzene-5-sulphonate (CHATTAWAY and MORRIS), 2017.
$C_{12}H_{11}O_3N_3S$ Ethyl penthian-4-one-3-carboxylate *p*-nitrophenylpyrazolone (BENNETT and SCORAH), 198.
$C_{12}H_{11}O_3N_2As$ Nitrodiphenylamine-6′-arsinic acids (GIBSON and JOHNSON), 2513.

$C_{12}H_{11}O_6N_2Cl$ Nitrobenzylpyridinium perchlorates (POLLARD and ROBINSON), 2778.

$C_{12}H_{12}ON_2S$ Ethyl penthian-4-one-3-carboxylate phenylpyrazolone (BENNETT and SCORAH), 198.

$C_{12}H_{12}O_4NAs$ Diphenylamine-*o*-arsinic acid (GIBSON and JOHNSON), 2507.

$C_{12}H_{13}O_3NS$ Acetyl-4-keto-2-methyltetrahydro-1:5-heptabenzthiazine (MILLS and WHITWORTH), 2749.

$C_{12}H_{14}O_2NCl$ 1-Chloroanilino*cyclo*pentane-1-carboxylic acids (OAKESHOTT and PLANT), 490.

$C_{12}H_{14}O_2NBr$ 1-Bromoanilino*cyclo*pentane-1-carboxylic acids (OAKESHOTT and PLANT), 490.

$C_{12}H_{14}O_2N_2Cl_2$ *n*-Butyl glyoxylate 2:4-dichlorophenylhydrazone (CHATTAWAY and BENNETT), 2851.

$C_{12}H_{15}ON_2Cl$ 1-Chloroanilino*cyclo*pentane-1-carboxyamides (OAKESHOTT and PLANT), 490.

$C_{12}H_{16}O_2NI$ 5:6-Dimethoxy-3:4-dihydro*iso*quinoline methiodide (HAWORTH), 2283.

$C_{12}H_{20}ONI$ *l*-Methylephedrine methiodide (SMITH), 2057.

12 V

$C_{12}H_4ONCl_2Br_3$ Dichlorotribromobenzoquinoneanil (BRADFIELD, COOPER, and ORTON), 2862.

$C_{12}H_4ONCl_3Br_2$ Trichlorodibromobenzoquinoneanil (BRADFIELD, COOPER, and ORTON), 2863.

$C_{12}H_4ONCl_2Br_4$ Trichlorotetrabromo-4-hydroxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2864.

$C_{12}H_5ONCl_2Br_3$ Dichlorotribromo-4-hydroxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2862.

$C_{12}H_5ONCl_3Br_2$ Trichlorodibromo-4-hydroxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2862.

$C_{12}H_7ONCl_3Br$ Trichlorobromo-4-hydroxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2863.

$C_{12}H_7O_2NCl_2S_2$ 2:5-Dichlorophenyl 2-nitrophenyl disulphide (BROOKER, CHILD, and SMILES), 1387.

$C_{12}H_7O_2NBr_2S_2$ 2:5-Dibromophenyl 2-nitrophenyl disulphide (BROOKER, CHILD, and SMILES), 1387.

$C_{12}H_8O_2N_2ClAs$ Chloronitrodihydrophenarsazines (GIBSON and JOHNSON), 2514.

$C_{12}H_8O_2N_2BrAs$ Bromonitro-5:10-dihydrophenarsazine (GIBSON and JOHNSON), 2514.

$C_{12}H_8O_4NClS_2$ 4-Chlorobenzenesulphonyl 2-nitrophenyl disulphide (BROOKER, CHILD, and SMILES), 1386.

$C_{12}H_9O_2N_2Cl_2As$ 2-Nitrodiphenylamine-6′-dichloroarsine (GIBSON and JOHNSON), 2513.

$C_{12}H_{11}ON_2BrS$ Ethyl penthian-4-one-3-carboxylate *p*-bromophenylpyrazolone (BENNETT and SCORAH), 198.

$C_{12}H_{17}O_2NBrI$ Trimethyl-6-bromo-*β*-piperonylethylammonium iodide (STEVENS), 184.

C_{13} Group.

$C_{13}H_{14}O_4$ 4-Methyl-5-*cyclo*hexane*spiro*-(0:1:2)-*dicyclo*pentan-3-one-1:2-dicarboxylic anhydride (INGOLD and SEELEY), 1688.

$C_{13}H_{16}O_2$ 3-Methoxy-4-ethoxystyryl methyl ketone (DICKINSON, HEILBRON, and IRVING), 1894.

$C_{13}H_{16}O_5$ 4-Methyl-5-*cyclo*hexane*spiro*-(0:1:2)-*dicyclo*pentan-3-one-1:2-dicarboxylic acid (INGOLD and SEELEY), 1688.

$C_{13}H_{18}O_3$ Ethyl benzyloxybutyrate (BENNETT and HOCK), 475.

$C_{13}H_{19}N$ 1-β-Phenylethylpiperidine, and its picrate (POLLARD and ROBINSON), 2779.

4-Phenyl-1-ethylpiperidine, and its hydrochloride (MILLS, PARKIN, and WARD), 2618.

$C_{13}H_{20}O$ 2-*iso*Propylidene-β-thujone (HUGH and KON), 2599.

$C_{13}H_{20}O_2$ *cyclo*Hexane*spiro*-2-ethyl*cyclo*hexane-3:5-dione (KON and NARAYANAN), 1542.

$C_{13}H_{20}O_5$ Ethyl 3:3-dimethyl*cyclo*pentan-2-one-1:4-dicarboxylate (GIBSON, HARIHARAN, and SIMONSEN), 3012.

$C_{13}H_{22}O_2$ Ethyl dehydroundecenoate, and its metallic derivatives (MYDDLETON and BERCHEM), 1928.

13 III

$C_{13}H_8OS_2$ 1:3-Benzdithiole-2-*p*-benzoquinone, and its hydrochloride (HURTLEY and SMILES), 536.

$C_{13}H_8O_2Cl_2$ 3:5-Dichloro-4-hydroxybenzophenone (BLAKEY, JONES, and SCARBOROUGH), 2868.

$C_{13}H_8O_2I_2$ 3:5-Di-iodo-4-hydroxybenzophenone (BLAKEY, JONES, and SCARBOROUGH), 2870.

$C_{13}H_8O_6N_2$ Dinitro-4-hydroxybenzophenones (BLAKEY, JONES, and SCARBOROUGH), 2871.

$C_{13}H_9O_2I$ 3-Iodo-4-hydroxybenzophenone (BLAKEY, JONES, and SCARBOROUGH), 2870.

$C_{13}H_9NSe$ Phenylbenzselenazole, and its chloroplatinate (CLARK), 2807.

$C_{13}H_{10}OS_2$ 2-*p*-Hydroxyphenyl-1:3-benzdithiole, and its nitrate (HURTLEY and SMILES), 536.

$C_{13}H_{10}O_4Cl_6$ Ethyl ester of anhydro-5-carboxy-2-ββ'β'-trichloro-α-hydroxyethoxy-1-ββ'β'-trichloro-α-hydroxyethylbenzene (CHATTAWAY and PRATS), 689.

$C_{13}H_{10}O_5N_4$ 3-Nitro-4-hydroxybenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 2380.

$C_{13}H_{10}O_6Cl_2$ ωω-Dichloro-5-carboxy-2-acetoxyacetophenone (CHATTAWAY and PRATS), 691.

$C_{13}H_{11}OAs$ 10-Methylphenoxarsine (AESCHLIMANN), 414.

$C_{13}H_{11}O_2N_3$ 3-Nitro-4-nitrosomethylaminodiphenyl (BELL and ROBINSON), 1130.

$C_{13}H_{11}O_4N_3$ 2:5-Dihydroxybenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 2340.

$C_{13}H_{11}O_4N_5$ 3-Nitro-4-aminobenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 23.

$C_{13}H_{11}O_7N_5$ 3:5-Diketo-2-*p*-nitrophenyltetrahydro-1:2:4-triazine-6-carboxylic acid urethane (WHITELEY and YAPP), 527.

$C_{13}H_{12}ON_2$ Harmine (MANSKE, PERKIN, and ROBINSON), 1.

$C_{13}H_{12}O_2N_2$ 3-Benzeneazo-2:6-dimethylpyrone (MULLEN and CROWE), 1753.

$C_{13}H_{13}O_4N_3$ 5-Methoxysalicylaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 2340.

$C_{13}H_{13}O_5N_4$ 3:5-Diketo-2-phenyltetrahydro-1:2:4-triazine-6-carboxylic acid urethane (WHITELEY and YAPP), 526.

$C_{13}H_{12}N_2S$ 2-Dimethylamino-β-naphthathiazole (HUNTER and STYLES), 1213.

$C_{13}H_{12}NAs$ 10-Methyl-5:10-dihydrophenarsazine (AESCHLIMANN), 416.

$C_{13}H_{13}O_2N$ Methylmethoxy-1-naphthaldoximes (BRADY and GOLDSTEIN), 1963.

$C_{13}H_{13}O_3As$ 10-Methylphenoxarsine dihydroxide (AESCHLIMANN), 414.

$C_{13}H_{13}O_6N_3$ Ethyl 2:4-dinitrophenylethylcyanoacetate, and its silver salt (FAIRBOURNE and FAWSON), 48.

$C_{13}H_{14}ON_2$ Harmaline (MANSKE, PERKIN, and ROBINSON), 1.

$C_{13}H_{14}O_3N_2$ Nitro-β-naphthyltrimethylamine, salts of (INGHAM), 1974.

$C_{13}H_{14}O_3N_2$ 10-Nitro-ψ-indoxyl*spirocyclo*hexane (BETTS, MUSPRATT, and PLANT), 1313.

$C_{13}H_{14}O_5N_2$ Ethyl hydrogen diketosuccinate tolylhydrazones (CHATTAWAY and HUMPHREY), 2794.

$C_{13}H_{14}O_7N_2$ 3-Nitro-4-acetamidobenzylidene diacetate (HODGSON and BEARD), 22.

$C_{13}H_{14}NI$ Lepidine alliodide (HAMER), 2802.

$C_{13}H_{14}N_2S$ *s*-α-Naphthyldimethylthiocarbamide (HUNTER and STYLES), 1213.

$C_{13}H_{15}ON$ ψ-Indoxyl*spirocyclo*hexane, and its sodium salt (BETTS, MUSPRATT, and PLANT), 1313.

*cyclo*Pentenylacetanilide (KON and NARAYANAN), 1547.

*cyclo*Pentylideneacetanilide (KON and NARAYANAN), 1547.

$C_{13}H_{15}O_4N$ 1-Carboxyanilino*cyclo*pentane-1-carboxylic acids (OAKESHOTT and PLANT), 493.

$C_{13}H_{15}O_5N$ Ethyl *p*-nitrobenzylacetoacetate (BURGESS), 2019.

$C_{13}H_{15}O_5Br$ 2-Bromo-4-methyl-5-*cyclo*hexane*spiro*-(0:1:2)*dicyclo*pentan-3-one-1:2-dicarboxylic acid (INGOLD and SEELEY), 1689.

$C_{13}H_{16}O_2N_2$ 5-Nitro-9-methylhexahydrocarbazole (GURNEY and PLANT), 1318.

$C_{13}H_{16}O_3N_2$ 1-Carboxyanilino*cyclo*pentane-1-carboxyamides (OAKESHOTT and PLANT), 492.

$C_{13}H_{17}O_2N$ 1-Anilino*cyclo*hexane-1-carboxylic acid (BETTS, MUSPRATT, and PLANT), 1312.

1-Toluidino*cyclo*pentane-1-carboxylic acids (OAKESHOTT and PLANT), 486.

Substance, from salicylaldehyde and β-hydroxylamino-βγ-dimethyl-Δγ-butene (EARL and KENNER), 2142.

$C_{13}H_{17}O_3N$ 1-*p*-Anisidino*cyclo*pentane-1-carboxylic acid (OAKESHOTT and PLANT), 488.

$C_{13}H_{17}O_3N_3$ 3:4-Dimethoxystyryl methyl ketone semicarbazone (DICKINSON, HEILBRON, and IRVING), 1892.

$C_{13}H_{18}ON_2$ 1-Anilino*cyclo*hexane-1-carboxylamide (BETTS, MUSPRATT, and PLANT), 1311.

$C_{13}H_{19}O_4N$ Methyl ethyl β-cyano-γ-methyl-Δ^δ-hexene-βζ-dicarboxylate (FARMER and HEALEY), 1065.

$C_{13}H_{20}NI$ Benzylmethylpiperidinium iodide (POLLARD and ROBINSON), 2776.

$C_{13}H_{21}O_3N_3$ 4-Methyl-5-*cyclo*hexane*spirocyclo*pentan-3-one-1-carboxylic acid semicarbazone (INGOLD and SEELEY), 1689.

$C_{13}H_{22}O_4N_6$ Methyl 4-hydroxy-2:2:3-trimethyl-Δ^3-*cyclo*hexen-5-one-1-carboxylate disemicarbazone (BHAGVAT and SIMONSEN), 83.

$C_{13}H_{25}O_2N_3$ 5-Acetyl-1:3:3:4-4-pentamethyl*cyclo*pentan-1-ol semicarbazones (VOGEL), 598.

13 IV

$C_{13}H_6ON_3Cl_3$ *cycloazi*-2:4:6-Trichlorophenylbenztriazone (CHATTAWAY and WALKER), 329.

$C_{13}H_7ON_3Cl_2$ *cycloazi*-2:4-Dichlorophenylbenztriazone (CHATTAWAY and WALKER), 328.

$C_{13}H_7ON_3Br_2$ 2:4-Dibromophenylbenztriazones (CHATTAWAY and WALKER), 329.

$C_{13}H_8ONCl_3$ 2:4:6-Trichlorobenzanilide (CHAPMAN), 1749.

$C_{13}H_8ON_3Br$ *p*-Bromophenylbenztriazones (CHATTAWAY and WALKER), 328.

$C_{13}H_8O_4N_2Cl_2$ 4:4′-Dichloro-3:3′-dinitrodiphenylmethane (LE FÈVRE and TURNER), 1120.

$C_{13}H_8O_7N_5Br$ 2:4:6-Trinitro-3-hydroxybenzaldehyde *p*-bromophenylhydrazone (HODGSON and BEARD), 2379.

$C_{13}H_9O_8N_5S$ *s*-Bis-3:5-dinitrophenylthiocarbamide (DYSON, GEORGE, and HUNTER), 444.

$C_{13}H_8N_2Br_4S$ *s*-Di-2:5-dibromophenylthiocarbamide (DYSON, GEORGE, and HUNTER), 443.

$C_{13}H_9ONCl_2$ *o*-Hydroxybenzylidenedichloroanilines (ROBERTS and TURNER), 1843.

$C_{13}H_9O_3N_3Cl_2$ 3:4-Dichlorobenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 25.

2:4-Dichlorodiazoaminobenzene-2′-carboxylic acid (CHATTAWAY and WALKER), 333.

$C_{13}H_9O_3N_3Br_2$ 3:4-Dibromobenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 26.

2:4-Dibromodiazoaminobenzene-2′-carboxylic acid (CHATTAWAY and WALKER), 332.

$C_{13}H_9O_3N_3I_2$ 3:4-Di-iodobenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 27.

$C_{13}H_9O_3N_3Br_2$ *β-o*-Nitrobenzoyl-2:4-dibromophenylhydrazine (CHATTAWAY and WALKER), 331.

$C_{13}H_9O_5N_4Br$ Dinitrohydroxybenzaldehyde *p*-bromophenylhydrazones (HODGSON and BEARD), 2379.

$C_{13}H_9O_4N_4Cl$ 4-Chloro-3-nitrobenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 24.

$C_{13}H_9O_4N_4Br$ 4-Bromo-3-nitrobenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 24.

$C_{13}H_9O_4N_4I$ 4-Iodo-3-nitrobenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 25.

$C_{13}H_{10}ONCl$ *o*-Hydroxybenzylidene-3-chloroaniline (ROBERTS and TURNER), 1843.

$C_{13}H_{10}ONAs$ 9-Methylcarbazole-3-arsenious oxide (BURTON and GIBSON), 2387.

$C_{13}H_{10}O_3Cl_2S_2$ 4-Toluenesulphonyl-2:5-dichlorophenyl disulphide (BROOKER, CHILD, and SMILES), 1386.

$C_{13}H_{10}O_3N_2Cl$ Chlorohydroxybenzaldehyde *p*-nitrophenylhydrazones (HODGSON and JENKINSON), 1741.

$C_{13}H_{10}O_3N_3Br$ Bromohydroxybenzaldehyde *p*-nitrophenylhydrazones (HODGSON and JENKINSON), 3041.

3-Nitro-4-hydroxybenzaldehyde *p*-bromophenylhydrazone (HODGSON and BEARD), 2380.

$C_{13}H_{10}O_3N_3I$ Iodohydroxybenzaldehyde *p*-nitrophenylhydrazones (HODGSON and JENKINSON), 3043.

$C_{13}H_{10}O_6N_2S$ *m*-Nitrophenylnitrobenzylsulphones (CHATTERJEE and ROBINSON), 2782.

$C_{13}H_{10}NCl_2As$ 9-Methylcarbazole-3-arsenious chloride (BURTON and GIBSON), 2387.

$C_{13}H_{10}N_2Br_2S$ *s*-Di-*o*-bromophenylthiocarbamide (DYSON, GEORGE, and HUNTER), 443.

$C_{13}H_{11}ON_3Br_2$ *o*-Aminobenzoyl-2:4-dibromophenylhydrazine (CHATTAWAY and WALKER), 330.

$C_{13}H_{11}O_4NS$ *m*-Nitrophenylbenzylsulphone (CHATTERJEE and ROBINSON), 2782.

$C_{13}H_{11}O_4NS_2$ 4-Toluenesulphonyl 2-nitrophenyl disulphide (BROOKER, CHILD, and SMILES), 1386.

$C_{13}H_{11}NClAs$ 10-Chloro-4-methyl-5:10-dihydrophenarsazine (GIBSON and JOHNSON), 2510.

$C_{13}H_{11}NBrAs$ 10-Bromomethyl-5:10-dihydrophenarsazines (GIBSON and JOHNSON), 2509.

$C_{13}H_{12}ONBr$ Aceto-4-bromo-2-methyl-α-naphthalide (SHOESMITH and RUBLI), 3103.

$C_{13}H_{12}O_3NAs$ Methylphenarsazinic acids, and their salts (GIBSON and JOHNSON), 2509.

$C_{13}H_{13}O_3NAs$ 9-Methylcarbazole-3-arsinic acid (BURTON and GIBSON), 2386.
$C_{13}H_{12}O_4N_2S$ *p*-Toluenesulphon-2-nitroanilide (BELL and ROBINSON), 1129.
$C_{13}H_{12}O_5NAs$ Carboxydiphenylamine-6′-arsinic acids (BURTON and GIBSON), 248.
$C_{13}H_{12}O_{13}N_4As_2$ *s*-Carbamido-5-nitro-4-amino-2-hydroxyphenylarsinic acid, and its salts (KING), 1056.
$C_{13}H_{12}N_2Br_4S$ 2-Dimethylamino-β-naphthathiazole tetrabromide (HUNTER and STYLES), 1213.
$C_{13}H_{14}O_3NAs$ Methyldiphenylaminearsinic acids (GIBSON and JOHNSON), 2508.
$C_{13}H_{14}O_9N_2As_2$ *s*-Carbamido-4-amino-2-hydroxyphenylarsinic acid (KING), 1055.
$C_{13}H_{15}ONS$ 3-Keto-2-benzyl-2:3-dihydro-1:4-benzthiazine (MILLS and WHITWORTH), 2748.
$C_{13}H_{15}O_3NS$ Ethyl 3-keto-2:3-dihydro-1:4-benzthiazine-2-propionate (MILLS and WHITWORTH), 2745.
Ethyl 4-ketotetrahydro-1:5-heptabenzthiazine-2-acetates (MILLS and WHITWORTH), 2743.
$C_{13}H_{16}O_9N_4As_2$ *s*-4-Carbamido-4:5-diamino-2-hydroxyphenylarsinic acid (KING), 1056.
$C_{13}H_{18}O_2N_2S$ Nitrophenyl β-piperidinoethyl sulphides (BENNETT and BERRY), 1680.
$C_{13}H_{18}O_5N_2S$ 1-*o*-Anisidino*cyclo*pentane-1-carboxyamide-5′-sulphonic acid, sodium salt (OAKESHOTT and PLANT), 488.
$C_{13}H_{19}O_2N_2I$ Nitrobenzylmethylpiperidinium iodides (POLLARD and ROBINSON), 2777.
$C_{13}H_{19}O_4N_2As$ 3-Acetamido-4-piperidinophenylarsinic acid (KING), 1053.

13 V

$C_{13}H_9O_2NClAs$ 10-Chloro-5:10-dihydrophenarsazinecarboxylic acids (BURTON and GIBSON), 249.
$C_{13}H_9O_2N_2ClBr$ Chlorobromobenzaldehyde *p*-nitrophenylhydrazones (HODGSON and BEARD), 25.
$C_{13}H_9O_2N_2ClI$ Chloroiodobenzaldehyde *p*-nitrophenylhydrazones (HODGSON and BEARD), 26.
$C_{13}H_9O_2N_2BrI$ Bromoiodobenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 26.
$C_{13}H_{10}O_4NClS_2$ 4-Toluenesulphonyl 4-chloro-2-nitrophenyl disulphide (BROOKER, CHILD, and SMILES), 1386.

13 VII

$C_{13}H_{28}O_4N_2Cl_4BrSPt$ Tetrachloro (triaminopropane-α-bromocamphor-π-sulphonate) platinum (MANN), 1231.

C_{14} Group.

$C_{14}H_{10}$ Phenanthrene, synthesis of (KENNER and WILSON), 1103.

14 II

$C_{14}H_8O_4$ Quinizarin, structure of (GREEN), 2384.
$C_{14}H_{10}O_2$ Benzil, surface tension and density of (GARNER and SUGDEN), 2882.
Dihydroxyanthracenes (GREEN), 555.
$C_{14}H_{10}O_5$ *o*-Benzoylphloroglucinaldehyde (ROBERTSON and ROBINSON), 1713.
Di-*p*-carboxydiphenyl ether, and its silver salt (REILLY, DRUMM, and BARRETT), 70.
1:3-Dihydroxy-7-methoxyxanthone (SHINODA), 1985.
$C_{14}H_{12}O_2$ 1-Methoxydiphenyl-1′-carboxylic acid (RULE and BRETSCHER), 926.
4-Methoxyphenyl benzoate (IRVINE and SMITH), 75.
$C_{14}H_{12}Br_2$ 2:2′-Dibromodibenzyl (KENNER and WILSON), 1111.
$C_{14}H_{14}O$ Di-*p*-tolyl ether (REILLY, DRUMM, and BARRETT), 67.
$C_{14}H_{14}O_2$ *iso*Hydrobenzoins (READ and STEELE), 917.

$C_{14}H_{14}Se$ Di-*o*-tolyl selenide (PORRITT), 29.
$C_{14}H_{16}Si$ Diphenyldimethylsilicane (KIPPING), 107.
$C_{14}H_{18}O_3$ 3-Methoxy-4-propoxystyryl methyl ketones (DICKINSON, HEILBRON, and IRVING), 1895.
$C_{14}H_{18}O_{10}$ Tetra-acetyl γ-mannolactone (GOODYEAR and HAWORTH), 3144.
$C_{14}H_{21}N$ 1-γ-Phenylpropylpiperidine, and its picrate (POLLARD and ROBINSON), 2780.
4-Phenyl-1-*n*-propylpiperidine, and its hydrochloride (MILLS, PARKIN, and WARD), 2619.
$C_{14}H_{24}O_4$ *dl-iso*Menthyl hydrogen succinate (READ, ROBERTSON, and COOK), 1233.

14 III

$C_{14}H_5O_9N_3$ Trinitrofluorenone-4-carboxylic acid (BELL and ROBINSON), 2238.
$C_{14}H_6O_7N_2$ 4:4′-Dinitrodiphenic anhydride (BELL and ROBINSON), 1697.
$C_{14}H_6O_{10}N_4$ 3:5:3′:5′-Tetranitrobenzil (CHATTAWAY and COULSON), 578.
$C_{14}H_7O_5N$ Nitrodiphenic anhydrides (BELL and ROBINSON), 1697, 2236.
Nitrofluorenone-4-carboxylic acid (BELL and ROBINSON), 2238.
$C_{14}H_8ON_4$ *p*-Azoxybenzonitrile (NISBET), 2084.
$C_{14}H_8O_3S$ Thionyldihydroxyanthracenes (GREEN), 557, 2344.
$C_{14}H_9O_3Cl$ 4-Chloro-1:9-dihydroxyanthracene (GREEN), 2343.
$C_{14}H_9O_3Cl$ Chlorohydroxybenzaldehyde benzoates (HODGSON and JENKINSON), 1741.
$C_{14}H_9O_3Br$ 4-Bromo-2-hydroxybenzaldehyde benzoate (HODGSON and JENKINSON), 3041.
$C_{14}H_9O_3I$ Iodohydroxybenzaldehyde benzoates (HODGSON and JENKINSON), 3043.
$C_{14}H_9O_6N_3$ Dinitrobenzylidenephenylnitromethane (BAKER and WILSON), 847.
2:4:4′-Trinitrostilbene (NISBET), 2082.
$C_{14}H_9O_8N_3$ Trinitro-4-methoxybenzophenones (BLAKEY, JONES, and SCARBOROUGH), 2872.
$C_{14}H_{10}O_2Cl_2$ 3:5-Dichloro-4-methoxybenzophenone (BLAKEY, JONES, and SCARBOROUGH), 2867.
$C_{14}H_{10}O_4N_2$ *p*-Nitrobenzylidenephenylnitromethane (BAKER and WILSON), 844.
$C_{14}H_{10}O_6N_2$ Dinitro-4-methoxybenzophenones (BLAKEY, JONES, and SCARBOROUGH), 2871.
$C_{14}H_{10}O_6Cu$ Cuprisalicylic acid, sodium salt (WARE), 1756.
$C_{14}H_{10}O_9N_4$ Tetranitrodi-*p*-tolyl ether (REILLY, DRUMM, and BARRETT), 73.
$C_{14}H_{10}NCl_3$ 2′:4:4′-Trichloro-3-acetamidodiphenyl (BLAKEY and SCARBOROUGH), 3004.
$C_{14}H_{11}O_2Cl$ 3-Chloro-4-methoxybenzophenone (BLAKEY, JONES, and SCARBOROUGH), 2867.
$C_{14}H_{11}O_2Br$ 3-Bromo-4-methoxybenzophenone (BLAKEY, JONES, and SCARBOROUGH), 2868.
$C_{14}H_{11}O_2I$ 3-Iodo-4-methoxybenzophenone (BLAKEY, JONES, and SCARBOROUGH), 2869.
$C_{14}H_{11}O_3Br$ Bromomethoxyphenyl benzoates (IRVINE and SMITH), 75.
$C_{14}H_{11}O_4N$ Nitro-4-methoxybenzophenones (BLAKEY, JONES, and SCARBOROUGH), 2870.
$C_{14}H_{11}O_5N_3$ Dinitro-3-acetamidodiphenyl (SCARBOROUGH and WATERS), 96.
Nitrobenzylnitrobenzaldoximes (BRADY and KLEIN), 879.
$C_{14}H_{11}O_7N_5$ 4:6-Dinitro-3-methoxybenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 2381.
$C_{14}H_{12}OS_2$ 2-*p*-Methoxyphenyl-1:3-benzdithiole, and its nitrate (HURTLEY and SMILES), 536.

$C_{14}H_{12}O_3N_2$ 5-Carboxy-2-ethoxyphenylglycollic acid phenylhydrazone (CHATTAWAY and PRATS), 690.

4′-Nitro-2-acetamidodiphenyl (SCARBOROUGH and WATERS), 96.

Nitro-3-acetamidodiphenyls (BLAKEY and SCARBOROUGH), 3008.

β-O-p-Nitrobenzylbenzaldoxime (BRADY and KLEIN), 885.

$C_{14}H_{12}O_4N_2$ 3-Nitro-4-methoxybenzanilide (BLAKEY, JONES, and SCARBOROUGH), 2870.

3-Nitro-4-methoxybenzophenoneoxime (BLAKEY, JONES, and SCARBOROUGH), 2870.

$C_{14}H_{12}O_5N_2$ Dinitrodi-*p*-tolyl ethers (REILLY, DRUMM, and BARRETT), 72.

$C_{14}H_{13}ON$ *N*-Methylbenziminophenyl ether (CHAPMAN), 1747.

$C_{14}H_{12}O_2Cl$ Chloro-2-benzyloxyanisoles (OXFORD and ROBINSON), 2241.

$C_{14}H_{13}O_3N$ Acetylmethoxy-1-naphthaldoximes (BRADY and GOLDSTEIN), 1962.

2-Nitrodi-*p*-tolyl ether (REILLY, DRUMM, and BARRETT), 72.

3-Nitrodi-*p*-tolyl ether (REILLY and BARRETT), 1399.

$C_{14}H_{13}O_6N$ Methyl nitrocinnamylidenemalonates (BAKER and ECCLES), 2128.

$C_{14}H_{14}ON_4$ Benzophenone δ-aminosemicarbazone (BROWN, PICKERING, and WILSON), 109.

$C_{14}H_{14}O_3N_2$ Quinoxaline derivative of 2:2-dimethyl*cyclo*pentane-3:4-dione-1-carboxylic acid (GIBSON, HARIHARAN, and SIMONSEN), 3014.

$C_{14}H_{14}O_4N_2$ 2:5-Dimethoxybenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 2340.

$C_{14}H_4O_5N_4$ 3:5-Diketo-2-*p*-tolyltetrahydro-1:2:4-triazine-6-carboxylic acid urethane (WHITELEY and YAPP), 527.

$C_{14}H_{14}NAs$ 10-Ethyl-5:10-dihydrophenarsazine (AESCHLIMANN), 416.

$C_{14}H_{15}ON$ Aminodi-*p*-tolyl ethers, and their salts (REILLY and BARRETT), 1400.

Diphenylhydroxyethylamines, and their salts (READ and STEELE), 910.

$C_{14}H_{15}N_3S$ Acetone δ-β-naphthylthiosemicarbazone (BAIRD, BURNS, and WILSON), 2533.

$C_{14}H_{16}O_3N_2$ Nitro-9-acetylhexahydrocarbazoles (GURNEY and PLANT), 1317.

10-Nitro-7-methyl-ψ-indoxyl*spirocyclo*hexane (BETTS, MUSPRATT, and PLANT), 1313.

$C_{14}H_{16}NBr$ 2:6-Dimethylquinoline allobromine (HAMER), 2801.

$C_{14}H_{16}NI$ 2:6-Dimethylquinoline alliodide (HAMER), 2800.

$C_{14}H_{16}N_2Se_2$ Di-*o*-methylaminodiphenyl diselenide (CLARK), 2807.

$C_{14}H_{17}ON$ 9-Acetyl-*trans*-hexahydrocarbazole (GURNEY, PERKIN, and PLANT), 2679.

$C_{14}H_{17}O_2N_3$ *iso*Nitroso-derivative of substance $C_{14}H_{18}ON_2$ (KRISHNAMURTI and DEY), 1351.

$C_{14}H_{17}O_4Br_3$ Substance, from bromine and dimethylpyrone (COLLIE and KLEIN), 2162.

$C_{14}H_{17}O_6N$ Indican, synthesis of (ROBERTSON), 1937.

$C_{14}H_{17}N_2Cl$ Dibenzylhydrazine hydrochloride (KENNER and WILSON), 1112.

$C_{14}H_{18}ON_2$ Substance, from benzoylacetonitrile, piperidine, and salicylaldehyde (KRISHNAMURTI and DEY), 1350.

$C_{14}H_{18}O_2N_2$ *meso*-1:4-Diacetyl-2:3-dimethyl-1:2:3:4-tetrahydroquinoxaline (GIBSON), 344.

1-*mm*′-Dimethoxyanilino-1-cyano*cyclo*pentane (OAKESHOTT and PLANT), 489.

$C_{14}H_{19}O_4N_3$ Ethyl nitropiperidinobenzoates (LE FÈVRE and TURNER), 1117.

$C_{14}H_{19}O_3N_3$ 3-Methoxy-4-ethoxystyryl methyl ketone semicarbazone (DICKINSON, HEILBRON, and IRVING), 1894.

$C_{14}H_{20}O_4N_2$ Ethyl βγ-dicyano-β-methylpentane-γε-dicarboxylate (GIBSON, HARIHARAN, and SIMONSEN), 3011.

$C_{14}H_{23}O_9N_3$ γ-*m*-Nitro-*p*-acetamidophenylpropyltrimethylamine, picrate of (Ingold and Wilson), 811.

$C_{14}H_{22}NI$ 4-Phenyl-1-methyl-1-ethylpiperidinium iodides (Mills, Parkin, and Ward), 2619.

$C_{14}H_{23}ON_3$ 2-*iso*Propylidene-β-thujone semicarbazone (Hugh and Kon), 2599.

β-Thujylideneacetone semicarbazone (Hugh and Kon), 2599.

$C_{14}H_{25}ON_3$ Acetone δ-*d*-bornylsemicarbazones (Goodson), 1998.

$C_{14}H_{25}O_4Br$ Ethyl α-bromo-$\beta\beta\beta'\beta'$-tetramethyladipate (Farmer and Kracovski), 684.

14 IV

$C_{14}H_7O_3ClS$ 4-Chloro-1:9-thionyldihydroxyanthracene (Green), 2344.

$C_{14}H_7O_4NCl_2$ Nitrodiphenic acid dichlorides (Bell and Robinson), 1697.

$C_{14}H_8O_2NCl_5$ Pentachloroacetoxydiphenylamine (Bradfield, Cooper, and Orton), 2858.

$C_{14}H_8O_6N_2S_2$ 3:3′-Dinitrobenzaldehyde disulphides (Hodgson and Beard), 2423.

$C_{14}H_9O_4N_2Cl$ 2′-Chloro-2:4-dinitrostilbene (Robinson and Zaki), 2489.

$C_{14}H_{10}O_3N_2Br_2$ 5:4′-Dibromo-3-nitro-4-acetamidodiphenyl (Bell and Robinson), 1130.

$C_{14}H_{10}O_5N_3Cl$ 3-Chloro-5:4′-dinitro-4-acetamidodiphenyl (Scarborough and Waters), 1137.

$C_{14}H_{10}O_6N_4S_2$ Dinitrodibenzaldehyde disulphide dioximes (Hodgson and Beard), 2424.

$C_{14}H_{10}O_7N_4Se$ Benzselenazole methopicrate (Clark), 2806.

$C_{14}H_{10}N_4Br_8S_2$ 3-Bromo-1-aminobenzthiazole tribromide (Dyson, Hunter, and Morris), 1192.

$C_{14}H_{11}ONBr_2$ 4:6-Dibromo-3-acetamidodiphenyl (Blakey and Scarborough), 3007.

$C_{14}H_{11}O_2NCl_2$ 3:5-Dichloro-4-methoxybenzanilide (Blakey, Jones, and Scarborough), 2868.

3:5-Dichloro-4-methoxybenzophenoneoxime (Blakey, Jones, and Scarborough), 2867.

$C_{14}H_{11}O_2N_2Br$ Phthalimidomethylpyridinium bromide (Kipping and Mann), 530.

$C_{14}H_{11}O_3N_2Cl$ Chloronitro-4-acetamidodiphenyl (Scarborough and Waters), 1137.

$C_{14}H_{11}O_3N_2Br$ 4-Bromo-4′-nitro-3-acetamidodiphenyl (Blakey and Scarborough), 3009.

4′-Bromo-3-nitro-4-acetamidodiphenyl (Scarborough and Waters), 1139.

5-Bromo-3-nitro-4-acetamidodiphenyl (Bell and Robinson), 1131.

$C_{14}H_{11}O_5N_4Br$ Dinitromethoxybenzaldehyde *p*-bromophenylhydrazone (Hodgson and Beard), 2381.

$C_{14}H_{12}ONCl$ Chloro-3-acetamidodiphenyls (Blakey and Scarborough), 3003.

Chloro-2-acetamidodiphenyls (Scarborough and Waters), 93.

$C_{14}H_{12}ONBr$ 5-Bromo-2-acetamidodiphenyl (Scarborough and Waters), 94.

Bromo-3-acetamidodiphenyls (Blakey and Scarborough), 3005.

$C_{14}H_{12}O_2NBr$ 3-Bromo-4-methoxybenzanilide (Blakey, Jones, and Scarborough), 2868.

3-Bromo-4-methoxybenzophenoneoximes (Blakey, Jones, and Scarborough), 2868.

$C_{14}H_{12}O_2NI$ 3-Iodo-4-methoxybenzanilide (Blakey, Jones, and Scarborough), 2869.

3-Iodo-4-methoxybenzophenoneoximes (Blakey, Jones, and Scarborough), 2869.

$C_{14}H_{12}O_3N_2Se_2$ Di-*o*-formylaminodiphenyl diselenide (Clark), 2808.

$C_{14}H_{12}O_3N_2Cl$ 4-Chloro-2-methoxybenzaldehyde *p*-nitrophenylhydrazone (Hodgson and Jenkinson), 1741.

$C_{14}H_{12}O_3N_2Br$ Bromomethoxybenzaldehyde *p*-nitrophenylhydrazones (Hodgson and Jenkinson), 3042.

$C_{14}H_{13}O_3N_2I$ Iodomethoxybenzaldehyde *p*-nitrophenylhydrazones (Hodgson and Jenkinson), 3043.

$C_{14}H_{13}O_4NCl$ 1:3-Dihydroxy-7-methoxyxanthonimine hydrochloride (Shinoda), 1984.

Nitrochloro-2-benzyloxyanisoles (Oxford and Robinson), 2241.

$C_{14}H_{12}O_4N_4S$ Nitromethylthiolbenzaldehyde *p*-nitrophenylhydrazones (Hodgson and Beard), 2426.

$C_{14}H_{12}O_5N_2S_2$ 4-Acetamidobenzenesulphonyl 2-nitrophenyl disulphide (Brooker, Child, and Smiles), 1386.

$C_{14}H_{13}NISe$ Phenylbenzselenazole methiodide (Clark), 2807.

$C_{14}H_{13}OSAs$ 10-Ethylphenoxarsine sulphide (Aeschlimann), 415.

$C_{14}H_{13}O_5NS_2$ 4-Methoxytoluene-3-sulphonyl 2-nitrophenyl disulphide (Brooker, Child, and Smiles), 1386.

$C_{14}H_{14}O_4N_2S$ *p*-Toluenesulphonmethyl-2-nitroanilide (Bell and Robinson), 1129.

$C_{14}H_{14}O_5N_2Br_2$ Ethyl diketosuccinate 2:4-dibromophenylhydrazone (Chattaway and Humphrey), 1326.

$C_{14}H_{15}O_2NS$ Phenylethanesulphonamides (Evans, Mabbott, and Turner), 1162.

$C_{14}H_{15}NIAs$ 10:10-Dimethyl-5:10-dihydrophenarsazonium iodide (Aeschlimann), 416.

$C_{14}H_{15}N_2ClBr$ Di-*o*-bromobenzylhydrazine hydrochloride (Kenner and Wilson), 1111.

$C_{14}H_{16}ONBr$ 6-Bromo-9-acetylhexahydrocarbazole, and its hydrobromide (Gurney and Plant), 1322.

$C_{14}H_{16}O_4N_4S_2$ Carbethoxymethyl-2-glyoxaline disulphide (Balaban and King), 1867.

$C_{14}H_{19}O_2N_2Br$ β-Phthalimidodimethyldiethylammonium bromide (Hanhart and Ingold), 1010.

$C_{14}H_{19}O_2N_2S$ Acetone *S*-*o*-carbethoxybenzylthiosemicarbazone (Baird, Burns, and Wilson), 2530.

C_{15} Group.

$C_{15}H_{10}O_5$ Carajuretin, and its salts (Chapman, Perkin, and Robinson), 3025.

$C_{15}H_{12}O_3$ 2:4-Dihydroxyphenyl styryl ketone (Ellison), 1723.

7-Hydroxyflavanone (Ellison), 1722.

$C_{15}H_{12}O_4$ Acetylbenzoylpyrocatechol (Green), 502.

$C_{15}H_{12}O_5$ Trihydroxyphenyl hydroxystyryl ketones (Ellison), 1723.

$C_{15}H_{12}S_3$ 2-Styryl-1:3-benzdithiole, and its nitrate (Hurtley and Smiles), 537.

$C_{15}H_{14}O_3$ Methyl 1-methoxydiphenyl-1-carboxylate (Rule and Bretscher), 926.

$C_{15}H_{16}O$ Di-*o*-tolylcarbinol (Boyd and Hatt), 908.

$C_{15}H_{18}O_7$ Ethyl 2:4:6-trimethoxybenzoylpyruvate (Pratt, Robertson, and Robinson), 1983.

$C_{15}H_{22}O_2$ Dehydrongaiene dioxides (McDowall), 737.

$C_{15}H_{22}O_{14}$ Tetracarbomethoxy γ-methylfructoside (Allpress, Haworth, and Inkster), 1234.

$C_{15}H_{24}O_2$ Dihydrongaiol (McDowall), 734.

Tetrahydrongaione (McDowall), 733.

$C_{15}H_{22}O_2$ Tetrahydrongaiene dioxide (McDowall), 740.

$C_{15}H_{26}O_2$ Tetrahydrongaiol (McDowall), 734.

15 III

$C_{15}H_9O_3Cl$ Chlorohydroxymethylanthraquinone (HAYASHI), 2524.

$C_{15}H_9O_3Br$ Bromohydroxymethylanthraquinone (HAYASHI), 2526.

$C_{15}H_9O_5N_3$ 2:5-Dinitrophenyloxazoles (INGHAM), 698.

$C_{15}H_9O_6N_7$ 3:5-Diketo-2-*o*-nitrophenyl-6-*o*-nitrobenzeneazotetrahydro-1:2:4-triazine (WHITELEY and YAPP), 527.

$C_{15}H_{10}ON_2$ *iso*Quinazindol-2-one (ASAHINA, MANSKE, and ROBINSON), 1709.

$C_{15}H_{10}O_3N_2$ 2-Phenyl-5-*m*-nitrophenyloxazole (INGHAM), 698.

$C_{15}H_{10}O_6N_2$ 2:4-Dinitro-3′:4′-methylenedioxystilbene (NISBET), 2082.

$C_{15}H_{10}N_4S$ *s*-Dicyanophenylthiocarbamides (DYSON, GEORGE, and HUNTER), 443.

$C_{15}H_{11}O_2N$ 3-Phenylindole-2-carboxylic acid (MANSKE, PERKIN, and ROBINSON), 7.

$C_{15}H_{11}O_2N_5$ 3:5-Diketo-6-benzeneazo-2-phenyltetrahydro-1:2:4-triazine (WHITELEY and YAPP), 527.

$C_{15}H_{11}O_2Cl$ 4′-Hydroxyflavylium chloride (IRVINE and ROBINSON), 2090.

$C_{15}H_{11}O_2I_3$ 4′-Hydroxyflavylium periodide (IRVINE and ROBINSON), 2090.

$C_{15}H_{11}O_3Cl$ Chrysinidin chloride (PRATT, ROBERTSON, and ROBINSON), 1977.

Dihydroxyflavylium chlorides (ROBERTSON and ROBINSON), 245, 2203.

$C_{15}H_{11}O_4Cl$ Apigenidin chloride ($+H_2O$) (PRATT, ROBERTSON, and ROBINSON), 1979.

Chlorohydroxybenzoyltoluic acids, and their salts (HAYASHI), 2520.

5:6:7-Trihydroxyflavylium chloride (CHAPMAN, PERKIN, and ROBINSON), 3040.

$C_{15}H_{11}O_4Br$ Bromohydroxybenzoyltoluic acids, and their salts (HAYASHI), 2525.

$C_{15}H_{11}O_5Cl$ Resomorinidin chloride (PRATT, ROBERTSON, and ROBINSON), 1982.

5:6:7:4′-Tetrahydroxyflavylium chloride (CHAPMAN, PERKIN, and ROBINSON), 3038.

$C_{11}H_{11}O_7N$ 2-Nitro-4:5-dimethoxyphenylpyruvic acid (OXFORD and RAPER), 418.

$C_{15}H_{11}O_7N_3$ 2:4:6-Trinitro-4′-methoxystilbene (NISBET), 2083.

$C_{15}H_{11}O_7Cl$ Chrysinidin perchlorate (PRATT, ROBERTSON, and ROBINSON), 1978.

$C_{15}H_{11}NS$ 1-Styrylbenzthiazole (MILLS and WHITWORTH), 2748.

$C_{15}H_{12}O_5N_2$ 2:4-Dinitro-2′-methoxystilbene (ROBINSON and ZAKI), 2489.

Nitrobenzyl-3:4-methylenedioxybenzaldoximes (BRADY and KLEIN), 880.

$C_{15}H_{13}O_2N$ Benzylidenepiperonylmethylamine, and its picrate (MALAN and ROBINSON), 2655.

$C_{15}H_{13}O_4N$ α-Phenylethyl *p*-nitrobenzoate (WARD), 453.

$C_{15}H_{13}O_5N_3$ *m*-Nitrobenzonitro-*m*-xylidides (DADSWELL and KENNER), 1107.

$C_{15}H_{13}O_5N_5$ 3-Nitro-4-acetamidobenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 23.

$C_{15}H_{13}O_6N_3$ Dinitrobenzamidophenetoles (FAWCETT and ROBINSON), 2420.

Nitrobenzylnitromethoxybenzaldoximes (BRADY and KLEIN), 881.

$C_{15}H_{13}NS$ 1-β-Phenylethylbenzthiazole (MILLS and WHITWORTH), 2749.

$C_{15}H_{14}O_2N_4$ Benzil δ-aminosemicarbazone (BROWN, PICKERING, and WILSON), 110.

$C_{15}H_{14}O_3N_2$ 5-Carboxy-2-hydroxyacetophenone, and its phenylhydrazone (CHATTAWAY and PRATS), 692.

3-Nitro-4-acetmethylamidodiphenyl (BELL and ROBINSON), 1130.

m-Nitrobenzo-*m*-xylidides (DADSWELL and KENNER), 1107.

$C_{15}H_{14}O_3N_4$ *p*-Acetamidobenzaldehyde *p*-nitrophenylhydrazone (HODGSON and BEARD), 22.

$C_{15}H_{14}O_4N_2$ Dinitrobenz-*p*-phenetidides (FAWCETT and ROBINSON), 2420.

Nitro-4-benzamidophenetoles (FAWCETT and ROBINSON), 2418.

Nitrobenzylmethoxybenzaldoximes (BRADY and KLEIN), 880.

$C_{15}H_{14}O_6N_2$ Nitro-3-methoxy-4-*p*-nitrobenzyloxytoluenes (OXFORD), 1967.
$C_{15}H_{15}N_3S$ Benzylidenebenzylthiosemicarbazide (BAIRD, BURNS, and WILSON), 2531.
$C_{15}H_{17}O_4N$ 7-Acetyl-ψ-indoxyl*spirocyclo*hexane (BETTS, MUSPRATT, and PLANT), 1312.
$C_{15}H_{17}O_8N$ 3-β-Glucosidoxyindole-2-carboxylic acid (ROBERTSON), 1940.
$C_{15}H_{17}O_8N_5$ Mesoxalyldiurethane nitrophenylhydrazones (WHITELEY and YAPP), 525.
$C_{15}H_{17}O_3N_3$ Substance, from *o*-phenylenediamine and α-keto-ββγγ-tetramethylglutaric hydroxylactone (ROTHSTEIN and SHOPPEE), 534.
$C_{15}H_{18}O_5N_2$ Ethyl diketosuccinate tolylhydrazones (CHATTAWAY and HUMPHREY), 2795.
$C_{15}H_{18}O_6N_4$ Mesoxalyldiurethane phenylhydrazone (WHITELEY and YAPP), 525.
$C_{15}H_{18}O_7N_2$ 3-β-Glucosidoxyindole-2-carboxylamide (ROBERTSON), 1940.
$C_{15}H_{23}O_2Cl$ Ngaiyl chloride, preparation of (MCDOWALL), 739.
$C_{15}H_{22}N_2S$ Benzylidene-δ-heptylthiosemicarbazide (BAIRD, BURNS, and WILSON), 2534.
$C_{15}H_{24}NI$ 4-Phenyl-1:1-diethylpiperidinium iodide (MILLS, PARKIN, and WARD), 2621.
$C_{15}H_{25}ON_3$ Methyl-β-thujylideneacetone semicarbazone (HUGH and KON), 2599.
$C_{15}H_{25}O_2N$ Ngaiylamine, and its salts (MCDOWALL), 738.
$C_{15}H_{28}O_2N_2$ Tetrahydrongaione hydrazone (MCDOWALL), 736.
$C_{15}H_{29}O_2N$ Tetrahydrongaiylamine, and its picrolonate (MCDOWALL), 734.

15 IV

$C_{15}H_{12}O_4N_2S$ *s*-Di-*o*-carboxyphenylthiocarbamide (DYSON, GEORGE, and HUNTER), 444.
$C_{15}H_{12}O_6N_2S$ *m*-Nitrophenyl β-(*p*-nitrobenzoyl)oxyethyl sulphide (BENNETT and BERRY), 1669.
$C_{15}H_{13}ONS$ *o*-Cinnamamidothiophenol (MILLS and WHITWORTH), 2746.
4-Keto-2-phenyltetrahydro-1:5-heptabenzthiazine (MILLS and WHITWORTH), 2745.
$C_{15}H_{13}O_2NS$ 2-Keto-2-phenyltetrahydro-1:5-heptabenzthiazine sulphoxide (MILLS and WHITWORTH), 2745.
$C_{15}H_{13}O_2N_3Br_2$ *o*-Acetamidobenzoyl-2:4-dibromophenylhydrazine (CHATTAWAY and WALKER), 331.
$C_{15}H_{13}O_3NS$ 4-Keto-2-phenyltetrahydro-1:5-heptabenzthiazine sulphone (MILLS and WHITWORTH), 2746.
$C_{15}H_{13}O_3N_2Br$ Nitrobenzoylbromoacetoxylidides (DADSWELL and KENNER), 1106.
$C_{15}H_{14}ONAs$ 5-Acetyl-10-methyl-5:10-dihydrophenarsazine (AESCHLIMANN), 416.
$C_{15}H_{14}O_3BrAs$ 10-Methyl-10-carboxymethylphenoxarsonium bromide (AESCHLIMANN), 415.
$C_{15}H_{15}O_4NS_2$ *m*-Carboxyphenylmethylsulphine-*p*-toluenesulphonylimine, resolution of, and its salts (CLARKE, KENYON, and PHILLIPS), 188.
$C_{15}H_{16}O_2N_2S$ *s*-Dianisylthiocarbamides (DYSON, GEORGE, and HUNTER), 440.
$C_{15}H_{17}O_2N_2Cl$ *o*-Nitrobenzylphenyldimethylammonium chloride (BAW), 1398.
$C_{15}H_{17}NIAs$ 10-Methyl-10-ethyl-5:10-dihydrophenarsazonium iodide (AESCHLIMANN), 416.

C_{16} Group.

$C_{16}H_{10}O_4$ 4-Hydroxy-3-benzoylcoumarin (HEILBRON and HILL), 1707.
$C_{16}H_{12}O_3$ 7-Hydroxy-2-phenyl-5-methylbenzopyrylium anhydro-base, and its salts (HIRST), 2493.
$C_{16}H_{12}O_3$ 4-Hydroxy-3-benzylcoumarin (HEILBRON and HILL), 1707.

$C_{16}H_{12}O_5$ Carajurone (CHAPMAN, PERKIN, and ROBINSON), 3027.
$C_{16}H_{12}N_2$ Dibenzodihydronaphthyridine, and its salts (HAWORTH and PINK), 2348.
$C_{16}H_{14}O$ *o-iso*Propenylbenzophenone (BARNETT, COOK, and NIXON), 509.
$C_{16}H_{14}O_2$ Phenyl 2-hydroxy-5-methoxystyryl ketone (IRVINE and ROBINSON), 2088.
$C_{16}H_{14}O_4$ 2:2′-Dimethoxybenzil, surface tension and density of (GARNER and SUGDEN), 2882.
$C_{16}H_{15}N$ 1-Benzyl-1:2:3:4-tetrahydro*iso*quinoline, and its sulphate (CHAKRAVARTI, HAWORTH, and PERKIN), 2277.
$C_{16}H_{16}O_2$ Dimethylphenylhydroxyphthalan (BARNETT, COOK, and NIXON), 509.
2-*p*-Tolyloxy-5-methylacetophenone (REILLY and DRUMM), 2819.
$C_{16}H_{21}N_2$ 2-Aminotetramethylbenzidine (BELL and ROBINSON), 1698.
$C_{16}H_{22}O_5$ Ethyl β-benzyloxyethylmalonate (BENNETT and HOCK), 475.
$C_{16}H_{24}O_6$ Tetramethylmannonic acid phenylhydrazide (GOODYEAR and HAWORTH), 3143.
$C_{16}H_{32}O_2$ Palmitic acid, sodium salt, effect of electrolytes on viscosity of (MCBAIN, WILLAVOYS, and HEIGHINGTON), 2689; hydrolysis of solutions of (MCBAIN and BUCKINGHAM), 2679.
Acid, from oxidation of *n*-triacontane (FRANCIS and WOOD), 1900.

16 III

$C_{16}H_9O_2Cl$ 2-*o*-Chlorobenzylidene-1:3-diketohydrindene (ROBINSON and ZAKI), 2488.
$C_{16}H_{10}ON_2$ Ketodibenzodihydronaphthyridine, and its salts (HAWORTH and PINK), 2347.
$C_{16}H_{10}O_4N_2$ *o*-Nitrobenzylidenehomophthalimide (HAWORTH and PINK), 2346.
$C_{16}H_{10}O_5N_4$ 3-Keto-2:5-dinitrophenyl-3:4-dihydro-1:4-diazines (INGHAM), 699.
$C_{16}H_{12}O_{12}N_8$ 1:4-Di-*oop*-trinitrophenylpiperazine (LE FÈVRE and TURNER), 1121.
$C_{16}H_{13}ON$ 2-Acetyl-3-phenylindole (MANSKE, PERKIN, and ROBINSON), 8.
$C_{16}H_{13}O_2Cl$ Methoxyflavylium chlorides (IRVINE and ROBINSON), 2088.
$C_{16}H_{13}O_3Cl$ Hydroxymethoxyflavylium chlorides (IRVINE and ROBINSON), 2091.
Scutellareinidin chloride methyl ether (CHAPMAN, PERKIN, and ROBINSON), 3038.
5:6:7:4′-Tetrahydroxy-4-methylflavylium chloride (CHAPMAN, PERKIN, and ROBINSON), 3035.
$C_{16}H_{13}O_6Cl$ Rhamnetinidin chloride (ROBERTSON and ROBINSON), 2206.
$C_{16}H_{14}ON_2$ Ketodibenzohexahydronaphthyridine, and its salts (HAWORTH and PINK), 2348.
$C_{16}H_{14}O_3N_2$ Nitrobenzylcinnamaldoximes (BRADY and KLEIN), 879.
$C_{16}H_{14}O_6N_4$ Ethyl 2:4-dinitrobenzoylformate phenylhydrazone (FAIRBOURNE and FAWSON), 49.
$C_{16}H_{14}O_6Cu$ Cuprimandelic acid, salts of (WARK), 1755.
$C_{16}H_{14}O_8N_8$ 1:4-Di-*op*-dinitrophenylpiperazine (LE FÈVRE and TURNER), 1121.
$C_{16}H_{15}O_2N$ Diacetyl-4-aminodiphenyl (SCARBOROUGH and WATERS), 1139.
$C_{16}H_{15}O_3N_3$ α-Phenylbutane-βγ-dione β-*m*-nitrophenylhydrazone (MANSKE, PERKIN, and ROBINSON), 7.
$C_{16}H_{15}O_4N_3$ 2:4-Dinitro-4′-dimethylaminostilbene, and its chloroplatinate (NISBET), 2083.
$C_{16}H_{15}O_6N_3$ Methyl *pp′*-dinitrodibenzylaminoformate (BAKER), 568.
$C_{16}H_{16}ON_2$ *p*-Acetamidobenzylidene-*p*-toluidine (HODGSON and BEARD), 22.
α-Phenylbutane-βγ-dione β-phenylhydrazone (MANSKE, PERKIN, and ROBINSON), 7.
$C_{16}H_{16}ON_4$ Benzaldehyde acetophenone carbohydrazone (BROWN, PICKERING, and WILSON), 109.

$C_{16}H_{16}O_2N_4$ Di-*p*-tolylformazylcarboxylic acid (WHITELEY and YAPP), 526.

$C_{16}H_{17}O_2N$ Methyl dibenzylaminoformate (BAKER), 568.

$C_{16}H_{17}O_3N$ *N*-*o*-Methoxybenzyl-*p*-methoxybenzaldoxime (BRADY and BENNETT), 896.

$C_{16}H_{17}N_3S$ Acetophenone δ-benzylthiosemicarbazone (BAIRD, BURNS, and WILSON), 2531.

Benzylidene-δ-α-phenylethylthiosemicarbazide (BAIRD, BURNS, and WILSON), 2532.

Dibenzyl ketone thiosemicarbazone (BAIRD and WILSON), 2117.

$C_{16}H_{18}O_4N_2$ Bisnitrosyl-*o*-methoxybenzyl (BRADY and BENNETT), 897.

$C_{16}H_{18}N_2Br_2$ Dibromohexadiene dipyridinium salt (FARMER, LAROIA, SWITZ, and THORPE), 2950.

$C_{16}H_{19}ON$ β-Amino-α-ethyl-αβ-diphenylethyl alcohol, and its hydrochloride (MCKENZIE and ROGER), 576.

$C_{16}H_{20}OSi$ Diethoxydiphenylsilicane (KIPPING and MURRAY), 2736.

$C_{16}H_{20}O_2N_2$ Acetamido-9-acetylhexahydrocarbazoles (GURNEY and PLANT), 1317.

$C_{16}H_{20}O_6N_4$ Mesoxalyldiurethane *p*-tolylhydrazone (WHITELEY and YAPP), 525.

$C_{16}H_{20}NCl$ Phenyl-α-phenylethyldimethylammonium chloride (EVANS, MABBOTT, and TURNER), 1163.

$C_{16}H_{22}ON_2$ Pinene nitrolanilide (EARL and KENNER), 1275.

$C_{16}H_{22}O_4N_4$ 4:6-Dinitro-1:3-dipiperidinobenzene (LE FÈVRE and TURNER), 1118.

$C_{16}H_{22}O_2N_2$ 1-Nitro-2:4-dipiperidinobenzene (LE FÈVRE and TURNER), 1117.

$C_{16}H_{23}O_3N$ Tetramethyladipanilic acids (FARMER and KRACOVSKI), 683.

$C_{16}H_{24}O_3S$ Menthyl benzenesulphonate, decomposition and rotation of (PATTERSON and MCALPINE), 350.

$C_{16}H_{28}O_6N_2$ Tetramethyl δ-galactonolactone phenylhydrazide (HAWORTH, HIRST, and JONES), 2430.

Tetramethyl mannonophenylhydrazide (DREW, GOODYEAR, and HAWORTH), 1243.

16 IV

$C_{16}H_8O_2N_4Cl_4$ Anhydrodiketosuccinic acid 2:4-dichlorophenylosazone (CHATTAWAY and HUMPHREY), 1327.

Dichlorophenyl-4:5-diketopyrazoline-3-carboxylic acid dichlorophenylhydrazone (CHATTAWAY and HUMPHREY), 1327.

$C_{16}H_8O_2N_4Br_4$ Anhydrodiketosuccinic acid 2:4-dibromophenylosazone (CHATTAWAY and HUMPHREY), 1325.

1-2′:4′-Dibromophenyl-4:5-diketopyrazoline-3-carboxylic acid 4-2″:4″-dibromophenylhydrazone (CHATTAWAY and HUMPHREY), 1325.

$C_{16}H_{10}O_2N_4Cl_2$ Anhydrodiketosuccinic acid chlorophenylosazone (CHATTAWAY and HUMPHREY), 1327.

Chlorophenyl-4:5-diketopyrazoline-3-carboxylic acid chlorophenylhydrazone (CHATTAWAY and HUMPHREY), 1328.

$C_{16}H_{10}O_2N_4Br_2$ Anhydrodiketosuccinic acid *p*-bromophenylhydrazone (CHATTAWAY and HUMPHREY), 1327.

1-*p*-Bromophenyl-4:5-diketopyrazoline-3-carboxylic acid 4-*p*-bromophenylhydrazone (CHATTAWAY and HUMPHREY), 1327.

$C_{16}H_{10}O_4N_4Cl_4$ Diketosuccinic acid 2:4-dichlorophenylosazone (CHATTAWAY and HUMPHREY), 1327.

$C_{16}H_{10}O_4N_4Br_4$ Diketosuccinic acid 2:4-dibromophenylosazone (CHATTAWAY and HUMPHREY), 1325.

$C_{16}H_{11}O_2N_4Br$ 1-Phenyl-4:5-diketopyrazoline-3-carboxylic acid 4-bromophenylhydrazone (CHATTAWAY and HUMPHREY), 2138.

$C_{16}H_{11}NClAs$ 7-Chloro-7:12-dihydro*iso*benzophenarsazine (GIBSON and JOHNSON), 2513.

$C_{16}H_{11}NBrAs$ 12-Bromo-7:12-dihydrobenzophenarsazine (GIBSON and JOHNSON), 2513.

$C_{16}H_{12}O_3NHS$ Benzophenarsazinic acids, and their salts (GIBSON and JOHNSON), 2511.

$C_{16}H_{12}O_4N_4Cl_2$ Diketosuccinic acid *p*-chlorophenylosazone (CHATTAWAY and HUMPHREY), 1327.

$C_{16}H_{12}O_4N_4Br_2$ Diketosuccinic acid *p*-bromophenylosazone (CHATTAWAY and HUMPHREY), 1327.

$C_{16}H_{12}O_5N_2As$ Benzoyloxy-1:4-dihydroquinoxaline-6-arsinic acids (EWINS, NEWBERY, and STICKINGS), 853.

$C_{16}H_{14}O_2N_2Br_2$ Succino-*p*-bromoanilide (BARNICOAT), 2928.

$C_{16}H_{14}O_3NBr$ Benzoyl-6-bromo-β-piperonylethylamine (STEVENS), 184.

$C_{16}H_{14}O_3NAs$ 2-Naphthylaminophenylarsinic acids (GIBSON and JOHNSON), 2511.

$C_{16}H_{15}O_4N_4Br$ Substance, from piperazine and 4:4′-dibromo-3:2′-dinitrodiphenyl (LE FÈVRE and TURNER), 1121.

$C_{16}H_{16}O_2N_2Se_2$ Di-*o*-formylmethylaminodiphenyl diselenide (CLARK), 2806.

$C_{16}H_{16}N_4Br_2S_2$ 1-Amino-5-methylbenzthiazole tribromide (DYSON, HUNTER, and MORRIS), 1192.

$C_{16}H_{18}O_4N_2Cl$ Di-*p*-nitrobenzyldimethylammonium chloride (STEDMAN), 1905.

$C_{16}H_{20}O_3NCl$ Chlorocamphoranilic acids (M. and R. SINGH), 1995.

$C_{16}H_{25}O_{12}N_3Co$ Aquo-2:6-dinitrophenoxobisethylenediamminocobaltic hydroxy-2:6-dinitrophenoxide (DUFF and BILLS), 2374.

16 V

$C_{16}H_{10}O_6N_2S_2Na_2$ Sodium *p*-sulphobenzeneazo-β-naphthyl sulphite (KING), 2644.

$C_{16}H_{11}O_4NCl_4S$ Anhydro-2-βββ-trichloro-α-hydroxyethoxy-1-ββδ-trichloro-α-hydroxyethylbenzene-5-sulphonanilide (CHATTAWAY and MORRIS), 2017.

C_{17} Group.

$C_{17}H_{10}O_4$ *iso*Benzanthragallol (CROSS and PERKIN), 1303.

Benzanthrapurpurin (CROSS and PERKIN), 1302.

*iso*Benzflavopurpurin (CROSS and BEVAN), 1305.

$C_{17}H_{12}O_4$ α-(6-Hydroxymethylpiperonyl)cinnamolactone (STEVENS and ROBERTSON), 2791.

$C_{17}H_{14}O$ Carajurin, and its salts (CHAPMAN, PERKIN, and ROBINSON), 3023.

$C_{17}H_{14}O_4$ 7-Acetoxyflavanone (ELLISON), 1722.

$C_{17}H_{14}O_5$ 3-(3′:4′-Dihydroxybenzylidene)-7-methoxychromanone (PERKIN, RÂY, and ROBINSON), 2097.

$C_{17}H_{16}O_2$ 1-Acetonyl-3-methyl-1:4-β-naphthapyran (DICKINSON and HEILBRON), 17.

7-Methoxy-2-phenyl-5-methylbenzopyrylium hydroxide, ferrichloride of (HIRST), 2494.

$C_{17}H_{16}O_3$ Phenyl 3:4-dimethoxystyryl ketone (DICKINSON, HEILBRON, and IRVING), 1896.

1:2:7-Trimethoxyanthracene (MACMASTER and PERKIN), 1309.

$C_{17}H_{16}O_4$ 3:4:6-Trimethoxyanthranol (MACMASTER and PERKIN), 1309.

$C_{17}H_{16}O_5$ 3-(3′:4′-Dihydroxybenzyl)-7-methoxychromanone (PERKIN, RÂY, and ROBINSON), 2098.

Phenacyl veratrate (MALAN and ROBINSON), 2656.

$C_{17}H_{17}N$ Tetrahydroprotoberberine, and its salts (CHAKRAVARTI, HAWORTH, and PERKIN), 2278.

$C_{17}H_{17}N_3$ 5-Keto-6-phenyl-2:3:4:5-tetrahydropyridine 5-phenylhydrazone (MANSKE, PERKIN, and ROBINSON), 10.

$C_{17}H_{21}N$ Benzyl-*n*-butylaniline, and its salts (REILLY and DRUMM), 1395.

$C_{17}H_{22}O_7$ Methyl ethyl hydrogen 4-methyl-5-*cyclo*hexane*spiro*-Δ^1-*cyclo*penten-3-one-1:2:4-tricarboxylate (INGOLD and SEELEY), 1688.

$C_{17}H_{22}N_2$ Benzyl-*n*-butyl-*p*-phenylenediamine, and its salts (REILLY and DRUMM), 1396.

$C_{17}H_{26}O_9$ Ethyl $\beta\delta$-dicarbethoxy-γ-ketopimelate (ROBINSON and ZAKI), 2413.

$C_{17}H_{30}O_4$ Tetrahydrongaiol acetate (MCDOWALL), 734.

17 III

$C_{17}H_{10}OS_2$ 1:3-Benzdithiole-2-β-naphthaquinone, and its hydrochloride (HURTLEY and SMILES), 536.

$C_{17}H_{11}O_4N_3$ 3-Nitrobenzaldehyde-4-azo-β-naphthol (HODGSON and BEARD), 23.

$C_{17}H_{12}O_2N_4$ 2:6-Dibenzeneazopyrone (MULLEN and CROWE), 1752.

$C_{17}H_{12}O_5Br$ Dibromocarajurin (CHAPMAN, PERKIN, and ROBINSON), 3024.

$C_{17}H_{13}ON$ Oxyprotoberberine (CHAKRAVARTI, HAWORTH, and PERKIN), 2279.

$C_{17}H_{13}O_3Cl$ Chlorohydroxydistyryl ketones (HEILBRON and HILL), 921.

$C_{17}H_{14}O_3N_4$ Methyl 1-phenyl-4:5-diketopyrazoline-3-carboxylate 4-phenylhydrazone (CHATTAWAY and HUMPHREY), 2139.

$C_{17}H_{14}O_5Br_4$ Carajurin tetrabromide (CHAPMAN, PERKIN, and ROBINSON), 3023.

$C_{17}H_{14}NCl$ Protoberberinium chloride (CHAKRAVARTI, HAWORTH, and PERKIN), 2279.

$C_{17}H_{14}NI$ Protoberberinium iodide (CHAKRAVARTI, HAWORTH, and PERKIN), 2279.

$C_{17}H_{15}O_2Cl$ 7-Methoxy-2-phenyl-5-methylbenzopyrylium chloride (HIRST), 2494.

$C_{17}H_{15}O_2N$ Ethyl 3-phenylindole-2-carboxylate (MANSKE, PERKIN, and ROBINSON), 7.

$C_{17}H_{15}O_2N_5$ 3:5-Diketo-6-*p*-toueneazo-2-*p*-tolyltetrahydro-1:2:4-triazine (WHITELEY and YAPP), 527.

$C_{17}H_{15}O_3Cl$ 3:4′-Dimethoxyflavylium chloride (ROBERTSON and ROBINSON), 2203.

7-Hydroxy-4′-methoxy-2-phenyl-5-methylbenzopyrylium chloride (HIRST), 2494.

$C_{17}H_{15}O_4Cl$ 3:5:4′-Trihydroxy-6:8-dimethylflavylium chloride (ROBERTSON and ROBINSON), 2204.

$C_{17}H_{15}O_5Cl$ 5:7-Dihydroxy-3′:4′-dimethoxyflavylium chloride (PRATT, ROBERTSON, and ROBINSON), 1981.

5:7-Dihydroxy-6:4′-dimethoxyflavylium chloride (CHAPMAN, PERKIN, and ROBINSON), 3039.

3:5:3′:4′-Tetrahydroxy-6:8-dimethylflavylium chloride (ROBERTSON and ROBINSON), 2205.

$C_{17}H_{15}O_7N_7$ Di-*o*-nitroformazylcarboxylic acid urethane (WHITELEY and YAPP), 526.

$C_{17}H_{17}O_3N_3$ *meso*-1-*p*-Nitrobenzoyl-2:3-dimethyl-1:2:3:4-tetrahydroquinoxaline (GIBSON), 344.

$C_{17}H_{17}O_5N_5$ Formazylcarboxylic acid urethane (WHITELEY and YAPP), 526.

$C_{17}H_{17}O_4N$ Piperonylmethyl-β-piperonylethylamine (MALAN and ROBINSON), 2656.

$C_{17}H_{17}O_6N_3$ 2-Nitro-4:5-dimethoxyphenylpyruvic acid phenylhydrazone (OXFORD and RAPER), 419.

$C_{17}H_{18}ON_2$ 1-Benzoyl-2:3-dimethyl-1:2:3:4-tetrahydroquinoxalines (GIBSON), 344.

$C_{17}H_{18}ON_4$ Diacetophenonecarbohydrazone (BROWN, PICKERING, and WILSON), 109.

$C_{17}H_{18}O_3N_2$ 5-Piperidino-2-nitrodiphenyl ether (LE FÈVRE, SAUNDERS, and TURNER), 1171.

$C_{17}H_{18}O_4N_4$ 4:6-Dinitro-3-anilino-1-piperidinobenzene (LE FÈVRE and TURNER), 1118.

$C_{17}H_{19}O_2N_3$ 4-Nitro-2-benzylideneaminodiethylaniline (BURTON and GIBSON), 2388.

$C_{17}H_{19}O_3N$ 2:6-Dimethoxy-4-methylbenz-*p*-toluidide (ROBERTSON and ROBINSON), 2200.

$C_{17}H_{19}O_3N_3$ Phenyl *β*-2-hydroxy-5-methoxyphenylethyl ketone semicarbazone (IRVINE and ROBINSON), 2093.

$C_{17}H_{19}O_5N$ Ethyl *δ*-phthalimido-*α*-acetylvalerate (MANSKE, PERKIN, and ROBINSON), 8.

$C_{17}H_{20}ON_2$ *p*-Nitrosobenzyl-*n*-butylaniline, and its hydrochloride (REILLY and DRUMM), 1396.

$C_{17}H_{20}N_2S$ *s*-Di-*m*-xylyl-2-thiocarbamide (DYSON, GEORGE, and HUNTER), 440.

$C_{17}H_{23}ON$ *α*-Ethyl-Δ^1-*cyclo*hexenylacet-*p*-toluidide (KON and NARAYANAN), 1540.

$C_{17}H_{28}NI$ 4-Phenyl-1:1-di-*n*-propylpiperidinium iodide (MILLS, PARKIN, and WARD), 2622.

17 IV

$C_{17}H_{10}O_3N_4Br_4$ Methyl 1-2′:4′-dibromophenyl-4:5-diketopyrazoline-3-carboxylate dibromophenyl hydrazone (CHATTAWAY and HUMPHREY), 1326.

$C_{17}H_{12}O_3N_4Br_2$ Methyl 1-*p*-bromophenyl-4:5-diketopyrazoline-3-carboxylate bromophenylhydrazone (CHATTAWAY and HUMPHREY), 1327.

$C_{17}H_{12}O_9N_2S_2$ Nitrobenzoylnaphthylaminedisulphonic acids, and their sodium salts (BALABAN and KING), 3078.

$C_{17}H_{12}O_{10}N_2S_2$ Nitrobenzoylamino-8-naphthol-3:6-disulphonic acids, salts (BALABAN and KING), 3090.

$C_{17}H_{13}O_{11}N_2S_3$ *m*-Nitrobenzoyl-1-naphthylamine-4:6:8-trisulphonic acid, salts (BALABAN and KING), 3095.

$C_{17}H_{14}O_4NBr$ Piperonylidene-6-bromo-*β*-piperonylethylamine (STEVENS), 184.

$C_{17}H_{14}O_7N_2S_2$ Aminobenzoylnaphthylaminedisulphonic acids, and their salts (BALABAN and KING), 3079.

$C_{17}H_{14}O_8N_2S_2$ *m*-Aminobenzoylamino-8-naphthol-3:6-disulphonic acids, and their salts (BALABAN and KING), 3090.

$C_{17}H_{15}O_2NS$ Acetyl-4-keto-2-phenyltetrahydro-1:5-heptabenzthiazine (MILLS and WHITWORTH), 2745.

$C_{17}H_{15}O_3N_3Br_2$ *o*-Acetamidobenzoyl-*α*-acetyl-2:4-dibromophenylhydrazine (CHATTAWAY and WALKER), 331.

$C_{17}H_{15}O_6N_4Br$ 4-Bromo-2:3′:5′-trinitro-4′-piperidinodiphenyl (LE FÈVRE, MOIR, and TURNER), 2338.

$C_{17}H_{16}O_3N_2Br_2$ Glutaro-*p*-bromoanilide (BARNICOAT), 2928.

$C_{17}H_{16}O_2N_2S$ *s*-Di-*p*-acetylphenylthiocarbamide (DYSON, GEORGE, and HUNTER), 442.

$C_{17}H_{16}O_3NBr$ Benzoylmethylbromopiperonylethylamine (STEVENS), 185.

$C_{17}H_{18}O_2N_4S$ *s*-Di-*p*-acetamidophenylthiocarbamide (DYSON, GEORGE, and HUNTER), 444.

$C_{17}H_{20}O_2N_2S$ *s*-Diethoxyphenylthiocarbamides (DYSON, GEORGE, and HUNTER), 441.

1-*p*-Toluenesulphonyl-2:3-dimethyl-1:2:3:4-tetrahydroquinoxalines (GIBSON), 345.

$C_{17}H_{20}O_4N_2S$ *s*-Bisdimethoxyphenylthiocarbamides (DYSON, GEORGE, and HUNTER), 441.

C_{18} Group.

$C_{18}H_{12}As_2$ Tri-*o*-phenylenediarsine (MCCLELAND and WHITWORTH), 2753.

$C_{18}H_{14}O_4$ Diacetoxyanthracenes (GREEN), 556.

ββ′-Diphenylmuconic acid (FARMER and DUFFIN), 411.

$C_{18}H_{14}O_6$ Diacetylflavopurpurin-anthranol (CROSS and PERKIN), 1304.

$C_{18}H_{16}O_2$ 4-Phenacyl-2-methyl-1:4-benzopyran (HEILBRON and HILL), 924.

$C_{18}H_{16}O_4$ *ββ′*-Diphenyl-Δ^{β}-dihydromuconic acids (FARMER and DUFFIN), 412.

$C_{18}H_{16}Br_2$ Dibromo-*αζ*-diphenylhexadiene (FARMER, LAROIA, SWITZ, and THORPE), 2955.

$C_{18}H_{16}Br_4$ Tetrabromo-$a\zeta$-diphenylhexatriene (FARMER, LAROIA, SWITZ, and THORPE), 2956.

$C_{18}H_{16}Br_6$ Hexabromo-$a\zeta$-diphenylhexatriene (FARMER, LAROIA, SWITZ, and THORPE), 2956.

$C_{18}H_{18}O_3$ 3-Methoxy-4-benzyloxystyryl methyl ketone (DICKINSON, HEILBRON, and IRVING), 1895.

$C_{18}H_{18}O_4$ *p*-Anisyl 4-hydroxy-2-methoxy-6-methylstyryl ketone (HIRST), 2495.

3:4:6:9-Tetramethoxyanthranol (MACMASTER and PERKIN), 1308.

$C_{18}H_{19}N$ Anhydromethyltetrahydroprotoberberine, and its hydrochloride (CHAKRAVARTI, HAWORTH, and PERKIN), 2280.

$C_{18}H_{20}O_2$ Diethylphenylhydroxyphthalan (BARNETT, COOK, and NIXON), 510.

$C_{18}H_{23}N$ Di(β-phenylethyl)dimethylamine, picrate of (HANHART and INGOLD), 1009.

$C_{18}H_{28}O_8$ Ethyl 2:3-dimethyl*cyclo*butane-1:1:4:4-tetracarboxylate (VOGEL), 1991.

$C_{18}H_{30}O_8$ Ethyl $\beta\gamma$-dimethylbutane-$aa\delta\delta$-tetracarboxylate (VOGEL), 1990.

$C_{18}H_{32}O_{16}$ Melezitose (LEITCH), 588.

$C_{18}H_{34}O_2$ Oleic acid, potassium hydrogen salt, crystalline (MCBAIN and STEWART), 1392.

18 III

$C_{18}H_{12}O_3As_2$ Tri-*o*-phenylenediarsine oxide (MCCLELAND and WHITWORTH), 2755.

$C_{18}H_{12}Br_4As_2$ Tri-*o*-phenylenediarsine tetrabromide (MCCLELAND and WHITWORTH), 2755.

$C_{18}H_{13}ON_3$ Rutæcarpine, synthesis of (ASAHINA, MANSKE, and ROBINSON), 1708.

$C_{18}H_{13}OAs$ 10-Phenylphenoxarsine (AESCHLIMANN), 415.

$C_{18}H_{13}O_2As$ 10-Phenylphenoxarsine oxide (AESCHLIMANN), 415.

$C_{18}H_{13}O_4Cl$ 4-Chloro-1:9-diacetoxyanthracene (GREEN), 2343.

$C_{18}H_{14}NAs$ 10-Phenyl-5:10-dihydrophenarsazine (AESCHLIMANN), 416.

$C_{18}H_{15}O_3Cl$ 4′-Chloro-2-methoxydistyryl ketone (HEILBRON and HILL), 923.

$C_{18}H_{15}O_4N$ 6:7-Methylenedioxy-2-piperonylmethyl-3:4-dihydro*iso*quinolinium hydroxide, picrate of (MALAN and ROBINSON), 2656.

$C_{18}H_{16}O_3N_4$ Anhydrodiketosuccinic acid tolylosazones (CHATTAWAY and HUMPHREY), 2795.

4:5-Diketo-1-tolylpyrazolinecarboxylic acid tolylhydrazones (CHATTAWAY and HUMPHREY), 2795.

$C_{18}H_{16}O_4As_2$ Phenylene-1:2-diphenylarsinic acid (MCCLELAND and WHITWORTH), 2754.

$C_{18}H_{17}O_2Cl$ 4′:7-Dimethoxy-2-phenyl-5-methylbenzopyrylium chloride (HIRST), 2494.

$C_{18}H_{17}O_4Cl$ 5:6:7-Trimethoxyflavylium chloride, and its ferrichloride (CHAPMAN, PERKIN, and ROBINSON), 3040.

$C_{18}H_{17}O_5Cl$ 5:7-Dihydroxy-6:4′-dimethoxy-4-methylflavylium chloride, and its ferrichloride (CHAPMAN, PERKIN, and ROBINSON), 3034.

7-Hydroxy-3:2′:4′-trimethoxyflavylium chloride (PRATT, ROBERTSON, and ROBINSON), 1982.

$C_{18}H_{17}O_5N$ *N*-Formylpiperonylmethyl-β-piperonylethylamine (MALAN and ROBINSON), 2656.

$C_{18}H_{18}O_4N_4$ Diketosuccinic acid tolylosazones (CHATTAWAY and HUMPHREY), 2795.

$C_{18}H_{19}O_3N$ 6-Methoxy-1-(3′-methoxybenzyl)-3:4-dihydro*iso*quinoline, and its picrate (CHAKRAVARTI, HAWORTH, and PERKIN), 2270.

$C_{18}H_{20}O_2N_6$ Diacetophenonehydrazidicarbohydrazone (BROWN, PICKERING, and WILSON), 111.

Dibenzoyl derivative of β-methyltrimethylenediamine (MANN), 2916.

$C_{18}H_{20}O_2N_2$ α-Phenylbutane-βγ-dione β-2:5-dimethoxyphenylhydrazone (MANSKE, PERKIN, and ROBINSON), 7.

$C_{18}H_{20}O_4N_2$ 4-Methoxy-*m*-oxalotoluidide (DADSWELL and KENNER), 585.

$C_{18}H_{20}NI$ Tetrahydroprotoberberine methiodides (CHAKRAVARTI, HAWORTH, and PERKIN), 2280.

$C_{18}H_{21}O_3N$ 6-Methoxy-1-(3′-methoxybenzyl)-1:2:3:4-tetrahydro*iso*quinoline, and its salts (CHAKRAVARTI, HAWORTH, and PERKIN), 2270.

$C_{18}H_{21}O_4N_3$ Diacetyl derivative of substance $C_{14}H_{18}ON_2$ (KRISHNAMURTI and DEY), 1351.

$C_{18}H_{23}ON$ β-Thujylideneacetanilide (HUGH and KON), 2598.

$C_{18}H_{31}ON_3$ Methyl*cyclo*hexanone δ-*d*-bornylsemicarbazones (GOODSON), 1999.

18 IV

$C_{18}H_{12}O_2N_4Cl_4$ Ethyl dichlorophenyldiketopyrazoline-3-carboxylate dichlorophenylhydrazone (CHATTAWAY and HUMPHREY), 1327.

$C_{18}H_{12}O_2N_4Br_4$ Ethyl dibromophenyl-4:5-diketopyrazoline-3-carboxylate dibromophenylhydrazone (CHATTAWAY and HUMPHREY), 1326.

$C_{18}H_{15}OClSi$ Phenoxydiphenylsilicyl chloride, and its action with sodium (KIPPING), 2728.

$C_{18}H_{14}O_2N_4Cl_2$ Ethyl chlorophenyl-4:5-diketopyrazoline-3-carboxylate chlorophenylhydrazone (CHATTAWAY and HUMPHREY), 1328.

$C_{18}H_{14}O_2N_4Br_2$ Ethyl 1-*p*-bromophenyl-4:5-diketopyrazoline-3-carboxylate bromophenylhydrazone (CHATTAWAY and HUMPHREY), 1327.

$C_{18}H_{16}O_4NBr$ 6:7-Methylenedioxy-2-piperonylmethyl-3:4-dihydro*iso*quinolinium bromide (MALAN and ROBINSON), 2656.

$C_{18}H_{18}O_2N_2Br_2$ Adipo-*p*-bromoanilide (BARNICOAT), 2928.

$C_{18}H_{19}O_3N_3S$ Benzaldehyde *S*-*o*-carbethoxybenzylthiosemicarbazone, and its hydrochloride (BAIRD, BURNS, and WILSON), 2530.

$C_{18}H_{20}O_2N_2S$ Thiodipropiondianilide (BENNETT and SCORAH), 196.

$C_{18}H_{20}O_6N_3As$ 3-*m*-Nitrobenzamido-4-piperidinophenylarsinic acid, and its salts (KING), 1054.

$C_{18}H_{22}O_4N_3As$ 3-*m*-Aminobenzamido-4-piperidinophenylarsinic acid, and its salts (KING), 1054.

$C_{18}H_{26}O_{16}N_{11}Co$ Aquopentamminocobaltic dinitrophenoxides (DUFF and BILLS), 2370.

$C_{18}H_{27}O_9N_8Co$ *p*-Nitrophenoxopentamminocobaltic *p*-nitrophenoxide (DUFF and BILLS), 2370.

18 V

$C_{18}H_{16}ON_2Cl_5Mo$ Diquinolinium molybdenyl pentachloride (JAMES and WARDLAW), 2148.

C_{19} Group.

$C_{19}H_{14}O_3$ 2-Phenyl-5-methyl-3:4-coumalo-6-benzopyran (HEILBRON and HILL), 924.

$C_{19}H_{14}O_4$ *iso*Benzanthragallol dimethyl ether (CROSS and PERKIN), 1303.
*iso*Benzflavopurpurin dimethyl ether (CROSS and BEVAN), 1306.

$C_{19}H_{16}O$ Benzhydryl phenyl ether (HEILBRON and HILL), 2011.

$C_{19}H_{18}O_5$ 9-Acetyl-3:4:6-trimethoxyanthranol (MACMASTER and PERKIN), 1309.

$C_{19}H_{18}O_7$ Quercetin tetramethyl ether (ATTREE and PERKIN), 239.

$C_{19}H_{20}O_5$ 3-Homoveratryl-7-methoxychromanone (PERKIN, RÂY, and ROBINSON), 2098.

$C_{19}H_{28}O_3$ Benzoyl-5-acetyl-1:3:3:4:4-pentamethyl*cyclo*pentan-1-ol (VOGEL), 599.

$C_{19}H_{30}O_{14}$ Tetracarbethoxymethylfructosides (ALLPRESS, HAWORTH, and INKSTER), 1235.

19 III

$C_{19}H_{14}O_3N_2$ Benzoyl-*o*-nitrodiphenylamine (CHAPMAN), 1748.

p-Nitrobenzoyldiphenylamine (CHAPMAN), 1749.

N-Phenylbenzimino-*p*-nitrophenyl ether (CHAPMAN), 1745.

$C_{19}H_{15}O_2N_3$ Benzenyl-*p*-nitrodiphenylamidine (CHEW and PYMAN), 2820.

$C_{19}H_{16}OS$ Dibenzylidenepenthianone (BENNETT and SCORAH), 199.

$C_{19}H_{16}O_3N_4$ 3:5-Dibenzeneazo-2:6-dimethylpyrone (MULLEN and CROWE), 1753.

$C_{19}H_{16}O_4N_2$ 6:7-Methylenedioxy-1-cyano-2-piperonylmethyl-1:2:3:4-tetrahydro*iso*quinoline (MALAN and ROBINSON), 2657.

$C_{19}H_{17}O_3N$ 3:11-Dimethoxyoxyprotoberberine (CHAKRAVARTI, HAWORTH, and PERKIN), 2273.

$C_{19}H_{17}O_4N_3$ Ethyl 1-phenyl-4-benzamido-5-ketopyrazoline-3-carboxylate (CHATTAWAY and HUMPHREY), 2136.

$C_{19}H_{18}O_3N_2$ 6-Nitro-9-benzoylhexahydrocarbazole (GURNEY and PLANT), 1321.

$C_{19}H_{18}O_3N_4$ *n*-Propyl 1-phenyl-4:5-diketopyrazoline-3-carboxylate 4-phenylhydrazone (CHATTAWAY and HUMPHREY), 2139.

$C_{19}H_{18}O_5Br_2$ Veratrylidene-7-methoxychromanone dibromide (PERKIN, RÂY, and ROBINSON), 2097.

$C_{19}H_{18}O_6N_2$ 6:7-Methylenedioxy-1-nitromethyl-2-piperonylmethyl-1:2:3:4-tetrahydro*iso*quinoline (MALAN and ROBINSON), 2657.

$C_{19}H_{18}O_8N_2$ Methyl di-*m*-nitrobenzylmalonate (BAKER and ECCLES), 2127.

$C_{19}H_{19}ON$ 9-Benzoyl-*trans*-hexahydrocarbazole (GURNEY, PERKIN, and PLANT), 2679.

$C_{19}H_{19}O_2N$ 3:11-Dimethoxydihydroprotoberberine, and its salts (CHAKRAVARTI, HAWORTH, and PERKIN), 2271.

$C_{19}H_{19}O_4Cl$ 5-Hydroxy-3:4′-dimethoxy-6:8-dimethylflavylium chloride (ROBERTSON and ROBINSON), 2204.

$C_{19}H_{19}O_5Cl$ 6-Hydroxy-5:7:4′-trimethoxy-4-methylflavylium chloride, and its ferrichloride (CHAPMAN, PERKIN, and ROBINSON), 3034.

5:6:7:4′-Tetramethoxyflavylium chloride, and its ferrichloride (CHAPMAN, PERKIN, and ROBINSON), 3037.

$C_{19}H_{19}O_6N$ 2-Carbomethoxyveratrylidenepiperonylmethylamine (MALAN and ROBINSON), 2655.

$C_{19}H_{21}O_3N$ 3:11-Dimethoxytetrahydroprotoberberine, and its salts (CHAKRAVARTI, HAWORTH, and PERKIN), 2271.

$C_{19}H_{21}O_3N_3$ 3-Methoxy-4-benzyloxystyryl methyl ketone semicarbazone (DICKINSON, HEILBRON, and IRVING), 1896.

$C_{19}H_{21}O_3N_5$ Di-*p*-tolylformazylcarboxylic acid urethane (WHITELEY and YAPP), 526.

$C_{19}H_{22}O_2N_2$ Glutarotoluidides (BARNICOAT), 2928.

$C_{19}H_{22}O_6N_2$ Veratrylidenemethoxychromanone oxamino-oxime (PERKIN, RÂY, and ROBINSON), 2097.

19 IV

$C_{19}H_9O_2NCl_7$ Heptachloro-4-benzoyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2859.

$C_{19}H_9ONCl_6$ *N*-2:4:6-Trichlorophenylbenzimino-2:4:6-trichlorophenyl ether (CHAPMAN), 1747.

$C_{19}H_9O_2NCl_6$ Hexachloro-4-benzoyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2858.

$C_{19}H_{10}O_2NCl_5$ 2:6:2′:4′:6′-Pentachloro-4-benzoyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2857.

$C_{19}H_{10}O_2NBr_5$ Pentabromo-4-benzoyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2861.

$C_{19}H_{11}O_2NCl_4$ 2:6:2′:4-Tetrachloro-4-hydroxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2857.

$C_{19}H_{11}ONCl_3$ Benzoyl-2:4:6-trichlorodiphenylamine (CHAPMAN), 1748.
N-2:4:6-Trichlorophenylbenziminophenyl ether (CHAPMAN), 1747.

$C_{19}H_{12}O_2NCl_3$ 2:2′:4′-Trichloro-4-benzoyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2857.

$C_{19}H_{13}ONCl_2$ Benzoyl-2:4-dichlorodiphenylamine (CHAPMAN), 1748.
3:5-Dichloro-2-benzamidodiphenyl (SCARBOROUGH and WATERS), 92.
N-2:4-Dichlorophenylbenziminophenyl ether (CHAPMAN), 1747.

$C_{19}H_{13}ONBr_2$ 3:5-Dibromo-2-benzamidodiphenyl (SCARBOROUGH and WATERS), 95.

$C_{19}H_{13}O_4N_2Br$ $\alpha\gamma$-Diphthalimido*iso*propyl bromide (MANN), 2912.

$C_{19}H_{14}ONCl$ 5-Chloro-2-benzamidodiphenyl (SCARBOROUGH and WATERS), 93.
Chlorobenzoyldiphenylamines (CHAPMAN), 1748.
Chlorophenylbenziminophenyl ethers (CHAPMAN), 1746.

$C_{19}H_{14}ONBr$ 5-Bromo-2-benzamidodiphenyl (SCARBOROUGH and WATERS), 94.

$C_{19}H_{14}O_2NCl$ 4′-Chloro-4-benzoyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2856.

$C_{19}H_{14}O_2NBr$ 4′-Bromo-4-benzoyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2860.

$C_{19}H_{16}OIAs$ 10-Phenyl-10-methylphenoxarsonium iodide (AESCHLIMANN), 415.

$C_{19}H_{16}O_5NBr$ 6′-Bromo-5:6-dimethoxy-3′:4′-methylenedioxy-1-benzoyl-3:4-dihydro*iso*quinoline (HAWORTH), 2284.

$C_{19}H_{17}O_2N_2I$ 2:2′-Dimethyloxacarbocyanine iodide (HAMER), 2803.

$C_{19}H_{17}NIAs$ 10-Phenyl-10-methyl-5:10-dihydrophenarsazonium iodide (AESCHLIMANN), 416.

$C_{19}H_{17}N_2IS_2$ 2:2′-Dimethylthiocarbocyanine iodide (HAMER), 2802.

$C_{19}H_{18}ONBr$ 6-Bromo-9-benzoylhexahydrocarbazole (GURNEY and PLANT), 1322.

$C_{19}H_{18}O_2NCl$ 3:11-Dimethoxyprotoberberinium chloride (CHAKRAVARTI, HAWORTH, and PERKIN), 2272.

$C_{19}H_{18}O_2NI$ 3:11-Dimethoxyprotoberberinium iodide (CHAKRAVARTI, HAWORTH, and PERKIN), 2272.

$C_{19}H_{18}O_4NBr$ 6′-Bromo-5:6-dimethoxy-3′:4′-methylenedioxy-1 benzyl-3:4-dihydro-*iso*quinoline (HAWORTH), 2284.

$C_{19}H_{20}O_2N_2Br_2$ Pimelo-*p*-bromoanilide (BARNICOAT), 2928.

$C_{19}H_{20}O_4N_2S$ *s*-Dicarbethoxyphenylthiocarbamides (DYSON, GEORGE, and HUNTER), 442.

$C_{19}H_{20}O_5BrN$ 6′-Bromo-3′:4′-methylenedioxyphenylaceto-β-2:3-dimethoxyphenylethylamide (HAWORTH), 2284.

19 V

$C_{19}H_8O_2NCl_3Br_4$ Trichlorotetrabromo-4-benzoyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2864.

$C_{19}H_{10}ONCl_3Br_2$ Trichlorodibromo-4-benzoyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2862.

$C_{19}H_{10}O_2NCl_3Br_2$ Dichlorotribromo-4-benzoyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2862.

$C_{19}H_{10}O_2NCl_7S$ Heptachlorobenzoquinoneanil (BRADFIELD, COOPER, and ORTON), 2859.

$C_{19}H_{11}O_2NCl_3Br$ Trichlorobromo-4-benzoyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2863.

$C_{19}H_{11}O_2NCl_4S$ Hexachloro-4-toluenesulphonyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2858.

$C_{19}H_{13}O_2NBr_5S$ Pentabromo-4-*p*-toluenesulphonyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2860.

$C_{19}H_{13}O_2NCl_5S$ 2:6:2′:4′:6′-Pentachloro-4-toluenesulphonyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2857.

$C_{19}H_{12}O_3NCl_4S$ 2:6:2′:4′-Tetrachloro-4-*p*-toluenesulphonyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2857.

$C_{19}H_{14}O_3NCl_3S$ 2:2′:4′-Trichloro-4-*p*-toluenesulphonyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2857.

$C_{19}H_{14}O_3NBr_2S$ Tribromo-4-*p*-toluenesulphonyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2860.

$C_{19}H_{16}O_2NBrS$ 4′-Bromo-4-*p*-toluenesulphonamidodiphenyl (BELL and ROBINSON), 1131.

19 VI

$C_{19}H_{12}O_3NCl_2Br_2S$ Dichlorotribromo-4-*p*-toluenesulphonyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2862.

$C_{19}H_{12}O_3NCl_3Br_2S$ Trichlorodibromo-4-*p*-toluenesulphonyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2862.

$C_{19}H_{13}O_3NCl_2BrS$ Trichlorobromosulphonyloxydiphenylamine (BRADFIELD, COOPER, and ORTON), 2863.

C_{20} Group.

$C_{20}H_{16}O_4$ Benzanthrapurpurin trimethyl ether (CROSS and PERKIN), 1302.

$C_{20}H_{16}O$ Benzhydryl *p*-tolyl ether (HEILBRON and HILL), 2011.

$C_{20}H_{26}S$ Di-*α*-phenylbutyl sulphide (EVANS, MABBOTT, and TURNER), 1167.

$C_{20}H_{32}O_{14}$ Tetracarbethoxy *γ*-ethylfructoside (ALLPRESS, HAWORTH, and INKSTER), 1236.

$C_{20}H_{38}O_{13}$ 2:3:4:5-Tetramethylgluconic acid (HAWORTH, LOACH, and LONG), 3154.

$C_{20}H_{40}O_2$ Acid, from oxidation of *n*-triacontane (FRANCIS and WOOD), 1900.

20 III

$C_{20}H_{10}O_8N_6$ 2:3-Di(3′:5′-dinitrophenyl)quinoxaline (CHATTAWAY and COULSON), 579.

$C_{20}H_{12}O_4N_4$ 2:3-Di(3′-nitrophenyl)quinoxaline (CHATTAWAY and COULSON), 578.

$C_{20}H_{12}O_8N_6$ 3:5:3′:5′-Tetranitrobenzil phenylhydrazone (CHATTAWAY and COULSON), 579.

$C_{20}H_{13}O_2N$ 4-Phthalimidodiphenyl (SCARBOROUGH and WATERS), 1140.

$C_{20}H_{14}O_5N_4$ 3:3′-Dinitrobenzil phenylhydrazone (CHATTAWAY and COULSON), 578.

$C_{20}H_{16}O_2N_2$ 2-Acetyl-3-*β*-phthalimidoethylindole (MANSKE, PERKIN, and ROBINSON), 11.

$C_{20}H_{16}O_4N_2$ *αγ*-Diphthalimido-*β*-methylpropane (MANN), 2915.

$C_{20}H_{17}O_2N$ *N*-Phenylbenziminoanisyl ethers (CHAPMAN), 1745.

Benzoylmethoxydiphenylamines (CHAPMAN), 1748.

$C_{20}H_{17}O_2N_3$ Benzenylmethyl-*p*-nitrophenylamidophenylimidine, and its salts (CHEW and PYMAN), 2321.

$C_{20}H_{17}O_3Cl$ 3-*o*-Hydroxyphenyl-5-chlorostyryl-Δ^5-*cyclo*hexen-1-ones (HEILBRON and HILL), 922.

$C_{20}H_{19}O_3N$ Anhydromethyl-3:11-dimethoxytetrahydroprotoberberine, and its hydrochloride (CHAKRAVARTI, HAWORTH, and PERKIN), 2274.

$C_{20}H_{19}O_3N_3$ *ζ*-Phthalimidohexane-*βγ*-dione *γ*-phenylhydrazone (MANSKE, PERKIN, and ROBINSON), 9.

$C_{20}H_{20}O_2N_4$ *n*-Butyl 1-phenyl-4:5-diketopyrazoline-3-carboxylate 4-phenylhydrazone (CHATTAWAY and HUMPHREY), 2139.

Ethyl 4:5-diketo-1-tolylpyrazolinecarboxylate tolylhydrazones (CHATTAWAY and HUMPHREY), 2796.

$C_{20}H_{20}O_4N_2$ *N*-Methyl-*N*-*β*-piperonylethyl-6-aminomethylhomopiperonylonitrile (STEVENS), 182.

$C_{20}H_{20}O_7N_2$ Ethyl bis-*p*-nitrobenzylacetoacetate (BURGESS), 2019.

$C_{20}H_{21}O_4N_3$ ζ-*o*-Carboxybenzamidohexane-βγ-dione γ-phenylhydrazone (MANSKE, PERKIN, and ROBINSON), 8.

$C_{20}H_{21}O_6Cl$ 5:6:7:4′-Tetramethoxy-4-methylflavylium chloride, and its ferrichloride (CHAPMAN, PERKIN, and ROBINSON), 3035.

$C_{20}H_{21}O_6N$ *N*-Methyl-*N*-β-piperonylethyl-6-aminomethylhomopiperonylic acid (STEVENS), 187.

$C_{20}H_{22}O_5N_2$ *N*-Methyl-*N*-β-piperonylethyl-6-aminomethylhomopiperonylamide (STEVENS), 183.

$C_{20}H_{24}O_2N_2$ Adipotoluidides (BARNICOAT), 2928.

$C_{20}H_{26}O_2S$ γγ′-Dibenzyloxydipropyl sulphide (BENNETT and HOCK), 480.

$C_{20}H_{26}O_3S$ Menthyl naphthalenesulphonates, rotation and decomposition of (PATTERSON and MCALPINE), 353.

$C_{20}H_{26}NI$ 4-Phenyl-1-benzyl-1-ethylpiperidinium iodides (MILLS, PARKIN, and WARD), 2621.

20 IV

$C_{20}H_{15}O_2N_2Bi$ Triphenylbismuthine dicyanate (CHALLENGER and WILSON), 211.

$C_{20}H_{15}O_2N_2Sb$ Triphenylstibine dicyanate (CHALLENGER and WILSON), 211.

$C_{20}H_{16}O_3N_4Br_4$ *n*-Butyl dibromophenyl-4:5-diketopyrazoline-3-carboxylate dibromophenylhydrazone (CHATTAWAY and HUMPHREY), 1326.

$C_{20}H_{16}O_6N_2Be$ Beryllium nitrobenzoylacetones (BURGESS), 2018.

$C_{20}H_{16}O_4N_2S$ 3-Nitro-4-*p*-toluenesulphonmethylamidodiphenyl (BELL and ROBINSON), 1129.

$C_{20}H_{18}O_4N_4Br_4$ Ethyl diketosuccinate 2:4-dibromophenylosazone (CHATTAWAY and HUMPHREY), 1326.

$C_{20}H_{19}O_4N_2Br$ *N*-Methyl-*N*-6′-bromo-β-piperonylethyl-6-aminomethylhomopiperonylonitrile, and its salts (STEVENS), 185.

$C_{20}H_{20}O_4N_2Cl$ ζ-*o*-Carboxybenzamidohexane-βγ-dione γ-*m*-chlorophenylhydrazone (MANSKE, PERKIN, and ROBINSON), 10.

$C_{20}H_{22}O_2N_2Br_2$ Subero-*p*-bromoanilide (BARNICOAT), 2928.

$C_{20}H_{23}O_5Cl_4Fe$ 5-Hydroxy-3:3′:4′-trimethoxy-6:8-dimethylflavylium ferrichloride (ROBERTSON and ROBINSON), 2204.

$C_{20}H_{24}O_2NCl$ 3:11-Dimethoxytetrahydroprotoberberine methochlorides (CHAKRAVARTI, HAWORTH, and PERKIN), 2274.

$C_{20}H_{24}O_2NI$ 3:11-Dimethoxytetrahydroprotoberberine methiodides (CHAKRAVARTI, HAWORTH, and PERKIN), 2273.

20 V

$C_{20}H_{12}O_6N_2S_2Na_2$ Sodium 4-sulpho-α-naphthalenazo-β-naphthyl sulphite (KING), 2644.

$C_{20}H_{20}O_4N_4Br_6S_2$ 1-Amino-5-carbethoxybenzthiazole tribromide (DYSON, HUNTER, and MORRIS), 1190.

C_{21} Group.

$C_{21}H_{12}O_5$ Benzoylalizarin (GREEN), 2931.

$C_{21}H_{14}O_3$ Benzo-β-naphtha*spiro*pyran (DICKINSON and HEILBRON), 1702.

$C_{21}H_{14}O_5$ 2:5-Dihydroxybenzaldehyde dibenzoate (HODGSON and BEARD), 2340.

$C_{21}H_{14}O_6$ Diacetyl*iso*benzanthragallol (CROSS and PERKIN), 1302.

Diacetyl*iso*benzflavopurpurin (CROSS and PERKIN), 1305.

$C_{21}H_{14}Cl_2$ 1:5-Dichloro-9-phenyl-10-methylene-9:10-dihydroanthracene (BARNETT, COOK, and WILTSHIRE), 1731.

$C_{21}H_{16}O_2$ 4-Hydroxy-2:2-diphenyl-Δ^3-chromen (HEILBRON and HILL), 2010.

$C_{21}H_{16}N_2$ Amino-2:4-diphenylquinolines (FAWCETT and ROBINSON), 2258.

$C_{21}H_{18}O_2$ 2-Benzoyldi-*p*-tolyl ether (REILLY and DRUMM), 2818.

$C_{21}H_{20}O_8$ Acetylquercetin tetramethyl ether (ATTREE and PERKIN), 239.

$C_{21}H_{20}O_{10}$ *iso*Quercitrin (ATTREE and PERKIN), 237.
$C_{21}H_{20}O_{12}$ Quercimeritrin (ATTREE and PERKIN), 237.
$C_{21}H_{24}O_{12}$ 4-*O*-Tetra-acetylglucosidoxy-2-hydroxybenzaldehyde (ROBERTSON and ROBINSON), 245.
$C_{21}H_{32}O_{11}$ Ethyl $\alpha\beta\beta'$-tricarbethoxy*iso*butyrylsuccinate (ROBINSON and ZAKI), 2413.
$C_{21}H_{40}O_{11}$ Methyl octamethyl cellobionate (HAWORTH, LONG, and PLANT), 2813.
Methyl octamethyl-lactobionate (HAWORTH and LONG), 547.

21 III

$C_{21}H_{15}OCl$ 2-Styryl-β-naphthapyrylium chloride (DICKINSON and HEILBRON), 18.
$C_{21}H_{15}O_2Cl$ 3-*p*-Hydroxystyryl-β-naphthapyrylium chloride ($+ 2H_2O$) (DICKINSON and HEILBRON), 18.
$C_{21}H_{15}O_3Cl$ 2-Chlorostyryl-5-methyl-3:4-coumalo-6-benzopyrans (HEILBRON and HILL), 921.
$C_{21}H_{17}O_2N$ Benzoyl-*p*-acetyldiphenylamine (CHAPMAN), 1748.
N-Phenylbenziminoacetylphenyl ethers (CHAPMAN), 1746.
$C_{21}H_{17}N_2Br_3$ *o*-Bromobenzylidene di-*o*-bromobenzylhydrazine (KENNER and WILSON), 1111.
$C_{21}H_{18}O_3N_4$ $\omega\omega$-Dichloro-5-carboxy-2-hydroxyacetophenone osazone (CHATTAWAY and PRATS), 691.
$C_{21}H_{18}O_4N_2$ 6-Methoxy-2-acetyl-3-β-phthalimidoethylindole (MANSKE, PERKIN, and ROBINSON), 13.
$C_{21}H_{18}N_2Br_2$ Benzylidenedi-*o*-bromobenzylhydrazine (KENNER and WILSON), 1111.
$C_{21}H_{19}O_2N$ 3-Benzoylaminodi-*p*-tolyl ether (REILLY and BARRETT), 1400.
$C_{21}H_{21}O_4N_3$ ζ-Phthalimidohexane-$\beta\gamma$-dione γ-*m*-methoxyphenylhydrazone (MANSKE, PERKIN, and ROBINSON), 12.
$C_{21}H_{21}O_5N$ Oxypalmatine (HAWORTH, KOEPFLI, and PERKIN), 553.
$C_{21}H_{21}O_6Cl$ 3-β-Glucosidoxy-7-hydroxyflavylium chloride (ROBERTSON and ROBINSON), 244.
$C_{21}H_{22}O_2N_2$ Normethylstrychnine (CLEMO, PERKIN, and ROBINSON), 1624.
Strychnine (OXFORD, PERKIN, and ROBINSON), 2380.
$C_{21}H_{22}O_5Br_4$ 3:3′:4:4′-Tetramethoxydistyryl ketone tetrabromide (DICKINSON, HEILBRON, and IRVING), 1892.
$C_{21}H_{22}O_3N_2$ ζ-*o*-Carboxybenzamidohexane-$\beta\gamma$-dione β-*m*-methoxyphenylhydrazone (MANSKE, PERKIN, and ROBINSON), 12.
$C_{21}H_{24}ON_2$ *iso*Strychnidine (OXFORD, PERKIN, and ROBINSON), 2404.
$C_{21}H_{24}O_2N_2$ Dihydrostrychnines (OXFORD, PERKIN, and ROBINSON), 2393.
$C_{21}H_{24}O_2N_2$ Strychnidone (CLEMO, PERKIN, and ROBINSON), 1613.
*allo*Strychnidone (CLEMO, PERKIN, and ROBINSON), 1615.
$C_{21}H_{25}ON_3$ Aminostrychnidine (OXFORD, PERKIN, and ROBINSON), 2408.
$C_{21}H_{25}O_2N_3$ Strychnidone oxime (CLEMO, PERKIN, and ROBINSON), 1614.
$C_{21}H_{25}O_4N$ Tetrahydropalmatine (HAWORTH, KOEPFLI, and PERKIN), 553.
$C_{21}H_{25}O_5N$ 3:11-Dimethoxytetrahydroprotoberberine methocarbonate (CHAKRAVARTI, HAWORTH, and PERKIN), 2274.
$C_{21}H_{26}ON_2$ Dihydrostrychnidines (OXFORD, PERKIN, and ROBINSON), 2399.
$C_{21}H_{26}O_2N_2$ Pimelotoluidides (BARNICOAT), 2928.
Tetrahydrostrychnine (CLEMO, PERKIN, and ROBINSON), 1600.
$C_{21}H_{26}O_4N_2$ Anhydromethoxymethylstrychnidonic acid (CLEMO, PERKIN, and ROBINSON), 1616.
Dioxyhydroxydihydrostrychnidine (OXFORD, PERKIN, and ROBINSON), 2407.
$C_{21}H_{28}O_2N_2$ Hexahydrostrychnine (OXFORD, PERKIN, and ROBINSON), 2403.

$C_{21}H_{28}O_5N_2$ Dioxyhydroxyhexahydrostrychnine (Oxford, Perkin, and Robinson), 2407.

Methoxymethylstrychnidonic acid (Clemo, Perkin, and Robinson), 1616.

$C_{21}H_{31}O_4N_5$ 2:4-Dinitro-1:3:5-tripiperidinobenzene (Le Fèvre and Turner), 1119.

$C_{21}H_{25}ON_3$ *iso*Pulegone δ-*d*-bornylsemicarbazone (Goodson), 1998.

21 IV

$C_{21}H_{16}O_{13}N_2S_4$ *s*-Carbamides of naphthylaminedisulphonic acids, sodium salts (Balaban and King), 3086.

$C_{21}H_{16}O_{15}N_2S_4$ *s*-Carbamide of 2:8-aminonaphthol-3:6-disulphonic acid, salts (Balaban and King), 3094.

$C_{21}H_{21}O_2N_2I$ 2:2′-Diethyloxacarbocyanine iodide (Hamer), 2803.

$C_{21}H_{21}N_2IS_2$ 2:2′-Diethylthiocarbocyanine iodide (Hamer), 2802.

$C_{21}H_{24}O_2N_2Br_2$ Azelo-*p*-bromoanilide (Barnicoat), 2928.

$C_{21}H_{25}ON_2I$ Strychnidine hydriodide (Clemo, Perkin, and Robinson), 1600.

$C_{21}H_{29}O_4NS$ Benzenesulphonngaiylamide (McDowall), 738.

C_{22} Group.

$C_{22}H_{16}O_2$ Methylbenzo-β-naphtha*spiro*pyrans (Dickinson and Heilbron), 1702.

$C_{22}H_{16}Cl_2$ 1:5-Dichloro-9-phenyl-10-ethylidene-9:10-dihydroanthracene (Barnett, Cook, and Wiltshire), 1731.

$C_{22}H_{18}O$ 2:2-Diphenylmethyl-Δ^3-chromens (Heilbron and Hill), 2010.

$C_{22}H_{18}O_2$ 4-Methoxy-2:2-diphenyl-Δ^3-chromen (Heilbron and Hill), 2010.

$C_{22}H_{18}O_4$ 2-*o*-Carboxybenzoyldi-*p*-tolyl ether and its silver salt (Reilly and Drumm), 2816.

$C_{22}H_{18}O_8$ Tetra-acetylflavopurpurin-anthranol (Cross and Perkin), 1305.

$C_{22}H_{16}N_2$ 8-Methoxy-2:3-diphenyl-5-methylquinoxaline (Dadswell and Kenner), 583.

$C_{22}H_{20}O_2$ 2:4-Diphenyl-3-methylchroman-2-ol (Heilbron and Hill), 2012.

Ethyl triphenylmethane-*o*-carboxylate (Barnett, Cook, and Nixon), 507.

$C_{22}H_{22}O$ Diphenyl-*o*-tolyl carbinyl ethyl ether (Boyd and Hatt), 906.

$C_{22}H_{22}O_4$ Ethyl ββ′-diphenylmuconate (Farmer and Duffin), 411.

$C_{22}H_{26}O_{11}$ ω-*O*-Tetra-acetyl-β-glucosidoxyacetophenone (Robertson and Robinson), 243.

$C_{22}H_{42}O_2$ *iso*Erucic acid, and its zinc salt (Mirchandani and Simonsen), 371.

22 III

$C_{22}H_{15}O_2Cl$ 3-3′:4′-Methylenedioxystyryl-β-naphthapyrylium chloride (Dickinson and Heilbron), 19.

$C_{22}H_{16}N_4S$ Di-β-naphthyliminotetrahydrothiodiazole (Baird, Burns, and Wilson), 2533.

$C_{22}H_{17}O_2Cl$ 3-*p*-Methoxystyryl-β-naphthapyrylium chloride (Dickinson and Heilbron), 18.

$C_{22}H_{17}O_3Cl$ 3-3′-Methoxy-4′-hydroxystyryl-β-naphthapyrylium chloride (+ $2H_2O$) (Dickinson and Heilbron), 18.

$C_{22}H_{18}O_8N_4$ Ethyl αβ-di-*p*-nitrophenyl-αβ-dicyanosuccinate (Fairbourne and Fawson), 49.

$C_{22}H_{16}N_4S_2$ Hydrazinedithiocarbo-β-naphthylamide (Baird, Burns, and Wilson), 2533.

$C_{22}H_{22}O_5Cu$ Copper hydroxymethylenacetoveratrone (Pratt, Robertson, and Robinson), 1981.

$C_{22}H_{23}O_{10}Cl$ 4′-β-Glucosidoxy-5:7-dihydroxy-3-methoxyflavylium chloride (Robertson and Robinson), 1714.

$C_{22}H_{34}O_{22}N_2$ 4:4:5-Trimethyl-Δ^5-*cyclo*pentene-1:3-dicarbanilides (BHAGVAT and SIMONSEN), 85.

$C_{22}H_{28}O_6N_6$ 2:5:3′-Trinitro-4:4′-dipiperidinodiphenyl (LE FÈVRE, MOIR, and TURNER), 2338.

$C_{22}H_{26}ON_2$ Methyl-ψ-strychnidine, and its salts (CLEMO, PERKIN, and ROBINSON), 1603.

$C_{22}H_{37}O_4N$ Anhydromethyltetrahydropalmatines (HAWORTH, KOEPFLI, and PERKIN), 2264.

$C_{22}H_{37}O_5N$ Cryptopalmatine, and its hydrochloride (HAWORTH, KOEPFLI, and PERKIN), 2264.

$C_{22}H_{37}O_7N$ Methyl N-β-veratrylethyl-3:4-dimethoxyhomophthalamate (HAWORTH, KOEPFLI, and PERKIN), 552.

$C_{22}H_{28}ON_2$ Methyldihydrostrychnidine, and its salts (CLEMO, PERKIN, and ROBINSON), 1621; (OXFORD, PERKIN, and ROBINSON), 2402.

$C_{22}H_{28}O_2N_2$ Subero-*o*-toluidide (BARNICOAT), 2928.

$C_{22}H_{28}O_4N_2$ Akuammine, and its salts (HENRY and SHARP), 1954.

22 IV

$C_{22}H_{16}O_5N_6Cl_4$ ωω-Dichloro-3:5-dinitro-2-ethoxyacetophenone osazone (CHATTAWAY and MORRIS), 2016.

$C_{22}H_{25}O_2N_2Br$ Strychnine methobromide (CLEMO, PERKIN, and ROBINSON), 1599.

$C_{22}H_{25}O_2N_2I$ Normethylstrychnine methiodide (CLEMO, PERKIN, and ROBINSON), 1625.

$C_{22}H_{26}O_3N_2Br_2$ Sebaco-*p*-bromoanilide (BARNICOAT), 2928.

$C_{22}H_{26}O_6N_4S$ 3:3′-Dinitro-4:4′-dipiperidinodiphenylsulphone (LE FÈVRE and TURNER), 1117.

$C_{22}H_{27}ON_2Cl$ Methyl*neo*strychnidinium chloride (CLEMO, PERKIN, and ROBINSON), 1611.

Strychnidine methochloride (CLEMO, PERKIN, and ROBINSON), 1601.

$C_{22}H_{27}ON_2Br$ Strychnidine methobromide (CLEMO, PERKIN, and ROBINSON), 1601.

$C_{22}H_{27}ON_2I$ Methyl*neo*strychnidinium iodide (CLEMO, PERKIN, and ROBINSON), 1611.

$C_{22}H_{27}O_2N_2I$ Dihydrostrychnine methiodides (OXFORD, PERKIN, and ROBINSON), 2395.

$C_{22}H_{27}O_{16}N_{10}Co$ Aquo-2:4-dinitrophenoxobisethylene diamminocobaltic 2:4-dinitrophenoxide (DUFF and BILLS), 2374.

$C_{22}H_{28}O_4NCl$ Tetrahydropalmatine methochlorides (HAWORTH, KOEPFLI, and PERKIN), 2263.

$C_{22}H_{28}O_4NI$ Tetrahydropalmatine methiodides (HAWORTH, KOEPFLI, and PERKIN), 2263.

$C_{22}H_{29}ON_2Cl$ Dihydrostrychnidine methochloride (OXFORD, PERKIN, and ROBINSON), 2401.

Methyl*neo*dihydrostrychnidinium chloride (CLEMO, PERKIN, and ROBINSON), 1623.

$C_{22}H_{29}ON_2I$ Dihydrostrychnidine methiodide (OXFORD, PERKIN, and ROBINSON), 2400.

Methyl*neo*dihydrostrychnidinium iodide (CLEMO, PERKIN, and ROBINSON), 1623.

$C_{22}H_{30}O_{10}N_7Co$ Aquo-*p*-nitrophenoxobisethylenediamminocobaltic *p*-nitrophenoxide (DUFF and BILLS), 2373.

C_{23} Group.

$C_{23}H_{16}O_7$ Triacetylbenzanthrapurpurin (CROSS and PERKIN), 1301.

$C_{23}H_{16}N_2$ 5:6-(2′:3′-Diphenylpyrrolo)(4′:5′)-quinoline, and its salts (FAWCETT and ROBINSON), 2256.

$C_{23}H_{18}O_2$ 1:2-Dibenzoyloxy-3-allylbenzene (PERKIN and TRIKOJUS), 1665.

$C_{23}H_{16}Cl_2$ 1:5-Dichloro-9-phenyl-10-propylanthracenes (BARNETT, COOK, and WILTSHIRE), 1731.

1:5-Dichloro-9-phenyl-10-propylidene-9:10-dihydroanthracene (BARNETT, COOK, and WILTSHIRE), 1731.

$C_{23}H_{20}O$ 2:2-Diphenyldimethyl-Δ^3-chromens (HEILBRON and HILL), 2011.

$C_{23}H_{22}O_2$ Diphenyl-2-hydroxy-β:4-dimethylstyrylcarbinol (HEILBRON and HILL), 2011.

$C_{23}H_{32}O_9$ *O*-Triacetyldihydrocarajurinol (CHAPMAN, PERKIN, and ROBINSON), 3024.

$C_{23}H_{28}O_5$ 3:3′-Dimethoxy-4:4′-diethoxydistyryl ketone (DICKINSON, HEILBRON, and IRVING), 1894.

$C_{23}H_{44}O_2$ Methyl *iso*erucate (MIRCHANDANI and SIMONSEN), 375.

23 III

$C_{23}H_{17}ON$ *N*-Phenylbenziminonaphthyl ethers (CHAPMAN), 1745.

$C_{23}H_{17}ON_3$ 9-Methylcarbazole-3-azo-β-naphthol (BURTON and GIBSON), 2386.

$C_{23}H_{17}O_3Cl$ *O*-Benzoylacacetinidin chloride ($+H_2O$) (PRATT, ROBERTSON, and ROBINSON), 1978.

$C_{23}H_{19}O_3Cl$ 3-3′:4′-Dimethoxystyryl-β-naphthapyrylium chloride (DICKINSON and HEILBRON), 19.

$C_{23}H_{20}O_6N_4$ Ethyl dibenzeneazochelidonate (MULLEN and CROWE), 1752.

$C_{23}H_{21}O_4Cl$ Ethyl 3-*o*-hydroxyphenyl-5-chlorostyryl-Δ^5-*cyclo*hexen-1-one-2-carboxylates (HEILBRON and HILL), 921.

$C_{23}H_{21}N_2I$ 1:1′-Dimethyl-4:4′-carbocyanine iodide (HAMER), 2801.

$C_{23}H_{22}O_7N_2$ Ethyl dibenzeneazoacetonedioxalate (MULLEN and CROWE), 1752.

$C_{23}H_{24}O_3N_2$ *O*-Acetyl*iso*strychnine (OXFORD, PERKIN, and ROBINSON), 2396.

$C_{23}H_{26}O_3N_2$ *O*-Acetyldihydro*iso*strychnine (OXFORD, PERKIN, and ROBINSON), 2398.

$C_{23}H_{26}O_4N_2$ Brucine methohydrogencarbonate (GULLAND, PERKIN, and ROBINSON), 1635.

$C_{23}H_{26}O_3N_2$ Brucidine and its salts (GULLAND, PERKIN, and ROBINSON), 1636.

$C_{23}H_{28}O_4N_4$ 3:3′-Dinitro-4:4′-dipiperidinodiphenylmethane (LE FÈVRE and TURNER), 1120.

$C_{23}H_{29}O_5N_3$ Tetrahydrobrucine nitrosoamine, and its hydrochloride (GULLAND, PERKIN, and ROBINSON), 1639.

$C_{23}H_{30}O_2N_2$ Azelotoluidides (BARNICOAT), 2928.

Methoxymethyldihydrostrychnidine (CLEMO, PERKIN, and ROBINSON), 1602.

n-Nonanedicarboxyanilide (BARNICOAT), 2928.

$C_{23}H_{30}O_3N_2$ Oxymethoxymethyl dihydrostrychnidines (CLEMO, PERKIN, and ROBINSON), 1604.

$C_{23}H_{30}O_3N_8$ Strychnidone disemicarbazone (CLEMO, PERKIN, and ROBINSON), 1614.

$C_{23}H_{30}O_4N_2$ Tetrahydrobrucine, and its salts (GULLAND, PERKIN, and ROBINSON), 1638.

$C_{23}H_{32}O_2N_2$ Methoxymethyltetrahydrostrychnidine, and its salts (CLEMO, PERKIN, and ROBINSON), 1617.

23 IV

$C_{23}H_{21}N_2BrS_2$ 2:2′-Diallylthiocarbocyanine bromide (HAMER), 2802.

$C_{23}H_{23}O_3N_3S$ 4-*p*-Sulphobenzeneazobenzyl-*n*-butylaniline, and its sodium salt (REILLY and DRUMM), 1396.

$C_{23}H_{23}O_3N_2Br_2$ *n*-Nonanedicarboxy-*p*-bromoanilide (BARNICOAT), 2928.

$C_{23}H_{28}O_6N_2S$ Strychnine methosulphate (CLEMO, PERKIN, and ROBINSON), 1599.

$C_{23}H_{29}ON_2I$ Methyl-ψ-strychnidine methiodide (CLEMO, PERKIN, and ROBINSON), 1610.

$C_{22}H_{30}O_5N_2S$ Strychnidine methosulphate (CLEMO, PERKIN, and ROBINSON), 1600.

*iso*Strychnidine methosulphate (OXFORD, PERKIN, and ROBINSON), 2405.

$C_{23}H_{30}O_6N_2S$ Dihydrostrychnine methosulphates (OXFORD, PERKIN, and ROBINSON), 2394.

$C_{23}H_{32}ON_2I_2$ Dihydrostrychnidine dimethiodide (OXFORD, PERKIN, and ROBINSON), 2402.

$C_{23}H_{32}O_5N_2S$ Dihydrostrychnidine methosulphate (OXFORD, PERKIN, and ROBINSON), 2400.

$C_{23}H_{33}O_7N_4AsS_2$ *s*-Carbamido-3-amino-4-piperidinophenylarsinic acid, and its magnesium salt (KING), 1054.

C_{24} Group.

$C_{24}H_{16}N_2$ Substance, from oxidation of carbazole (MCLINTOCK and TUCKER), 1221.

$C_{24}H_{18}N_2$ 6-Methoxyphenacylideneflavene (IRVINE and ROBINSON), 2093.

$C_{24}H_{22}O_4$ 2-Hydroxy-5-methoxybenzylidenediacetophenone (IRVINE and ROBINSON), 2088.

4-Methoxy-2:2-dianisyl-Δ^3-chromen (HEILBRON and HILL), 2010.

$C_{24}H_{26}N_6$ 3-*mp*-Dimethoxyphenyl-5-*mp*-dimethoxystyryl-Δ^5-*cyclo*hexen-1-one (DICKINSON, HEILBRON, and IRVING), 1892.

$C_{24}H_{28}N_2$ 6β-*pp'*-Tetramethyldiaminodiphenylstyrene and its dihydrochloride (RODD and LINCH), 2185.

$C_{24}H_{28}O_6$ 3:4-Dimethoxystyryl methyl ketone, dimeride (DICKINSON, HEILBRON, and IRVING), 1893.

$C_{24}H_{29}N_2$ *pp'*-Tetramethyldiaminodiphenyl-*o*-tolylmethylamine (RODD and LINCH), 2177.

24 III

$C_{24}H_{12}N_2Br_4$ 3:6:3':6'-Tetrabromo-9:9'-dicarbazyl (MCLINTOCK and TUCKER), 1216.

$C_{24}H_{12}N_2I_4$ 3:6:3':6'-Tetraiodo-9:9'-dicarbazyl (MCLINTOCK and TUCKER), 1218.

$C_{24}H_{12}O_{12}N_2$ 4:4'-Bis-*op*-dinitrophenyl-2:2'-dinitrodiphenylamine (LE FÈVRE, MOIR, and TURNER), 2337.

$C_{24}H_{17}O_5N_3$ Dibenzoyl-1-phenyl-4-amino-5-ketopyrazoline-3-carboxylic acid (CHATTAWAY and HUMPHREY), 2136.

$C_{24}H_{16}ON_2$ 2-Keto-1-methyl-5:6-(2':3'-diphenylpyrrole)(4':5')-1:2-dihydroquinoline (FAWCETT and ROBINSON), 2257.

Ketophenylethyldibenzodihydronaphthyridine (HAWORTH and PINK), 2347.

$C_{24}H_{18}O_2N_2$ 1:8-Naphthaldianilide (DAVIES and LEEPER), 1127.

$C_{24}H_{16}O_4N$ *o*-Nitrobenzylidene-*N*-β-phenylethylhomophthalimide (HAWORTH and PINK), 2347.

$C_{24}H_{16}O_4N_2$ *o*-Nitrobenzylidene-*N*-β-phenylethylhomophthalimide (HAWORTH and PINK), 2347.

$C_{24}H_{20}O_2Si$ Diphenoxydiphenylsilicane (KIPPING), 2731.

$C_{24}H_{20}O_6N_4$ *meso*-1:4-Di-*m*-nitrobenzoyl-2:3-dimethyl-1:2:3:4-tetrahydroquinoxaline (GIBSON), 344.

$C_{24}H_{22}ON_2$ Ketophenylethyldibenzohexahydronaphthyridine (HAWORTH and PINK), 2348.

$C_{24}H_{22}O_2N_2$ *meso*-1:4-Dibenzoyl-2:3-dimethyl-1:2:3:4-tetrahydroquinoxaline (GIBSON), 344.

$C_{24}H_{23}O_4Cl$ Ethyl 3-*o*-methoxyphenyl-5-*p*-chlorostyryl-Δ^5-*cyclo*hexen-1-one-2-carboxylate (HEILBRON and HILL), 923.

$C_{24}H_{24}O_2N_4$ *meso*-1:4-Diphenylcarbamyl-2:3-dimethyl-1:2:3:4-tetrahydroquinoxaline (GIBSON), 345.

$C_{24}H_{26}ON_2$ Benzoylbenzyl-*n*-butyl-*p*-phenylenediamine (REILLY and DRUMM), 1396.

$C_{24}H_{27}O_{10}Cl$ 7-Glucosidoxy-3:3′:4′-trimethoxyflavylium chloride (+H_2O) (ROBERTSON), 246.

$C_{24}H_{27}O_{11}N$ Penta-acetylindican (ROBERTSON), 1941.

$C_{24}H_{27}O_{12}N$ Methyl 3-tetra-acetyl-β-glucosidoxyindole-2-carboxylate (ROBERTSON), 1939.

$C_{24}H_{28}O_2N_2$ *pp′*-Tetramethyldiaminodiphenyl-*p*-anisylcarbinol (RODD and LINCH), 2177.

pp′-Tetramethyldiaminodiphenylbenzylcarbinol (RODD and LINCH), 2184.

pp′-Tetramethyldiaminodiphenyl-*o*-tolylcarbinol (RODD and LINCH), 2177.

$C_{24}H_{30}O_3N_2$ Methyl-ψ-brucidine, and its salts (GULLAND, PERKIN, and ROBINSON), 1651.

$C_{24}H_{30}O_4N_4$ 4:4′-Dibromo-3:3′-dinitro-*s*-diphenylethane (LE FÈVRE and TURNER), 1120.

$C_{24}H_{30}O_5N_2$ Acetylakuammine, and its salts (HENRY and SHARP), 1957.

$C_{24}H_{31}O_5N_5$ Brucidone semicarbazone (GULLAND, PERKIN, and ROBINSON), 1652.

$C_{24}H_{32}O_2N_2$ *n*-Decanedicarboxyanilide (BARNICOAT), 2928.

Ethoxymethyldihydrostrychnidine (CLEMO, PERKIN, and ROBINSON), 1616.

Sebacotoluidides (BARNICOAT), 2928.

$C_{24}H_{32}O_3N_2$ Methyl-ψ-dihydrobrucidine, and its dihydriodide (GULLAND, PERKIN, and ROBINSON), 1661.

$C_{24}H_{32}O_4N_2$ Brucidine methoxyhydroxide (+$2H_2O$) (GULLAND, PERKIN, and ROBINSON), 1641.

$C_{24}H_{34}O_3N_2$ Methoxymethyldihydrostrychnidine methohydroxide (CLEMO, PERKIN, and ROBINSON), 1605.

24 IV

$C_{24}H_{17}O_4N_4Br$ Substance, from benzidine and 4:4′-dibromo-3:3′-dinitrodiphenyl (LE FÈVRE and TURNER), 1121.

$C_{24}H_{17}O_{10}N_3S_2$ Nitrobenzoylaminobenzoylnaphthylamine-3:6-disulphonic acids, and their salts (BALABAN and KING), 3079.

$C_{24}H_{17}O_{11}N_3S_2$ 2-*m′*-Nitrobenzoyl-*m*-aminobenzoylamino-8-naphthol-3:6-disulphonic acid, salts (BALABAN and KING), 3093.

$C_{24}H_{17}O_{11}N_3S_2$ 1-*m′*-Nitrobenzoyl-*m*-aminobenzoylamino-8-naphthol-3:6-disulphonic acid, sodium salt (BALABAN and KING), 3091.

$C_{24}H_{17}O_{12}N_3S_3$ *m′*-Nitrobenzoyl-*m*-aminobenzoyl-1-naphthylamine-4:6:8-trisulphonic acid, salts (BALABAN and KING), 3095.

$C_{24}H_{19}O_3Cl_4Fe$ 6-Methoxy-4-phenacylflavylium ferrichloride (IRVINE and ROBINSON), 2093.

$C_{24}H_{19}O_8N_3S_2$ Diaminobenzoyl-2-naphthylamine-5:7-disulphonic acids, and their salts (BALABAN and KING), 3082.

$C_{24}H_{19}O_9N_3S_2$ *m′*-Aminobenzoyl-*m*-aminobenzoylamino-8-naphthol-3:6-disulphonic acids, sodium salts (BALABAN and KING), 3091.

$C_{24}H_{19}O_{11}N_3S_3$ Diaminobenzoyl-1-naphthylamine-4:6:8-trisulphonic acid, sodium salts (BALABAN and KING), 3096.

$C_{24}H_{20}N_2ClBr_3$ Tri-*o*-bromobenzylhydrazine hydrochloride (KENNER and WILSON), 1111.

$C_{24}H_{23}O_2N_2I$ Methoxymethyldihydrostrychnidine methiodide (CLEMO, PERKIN, and ROBINSON), 1604.

$C_{24}H_{30}O_2N_2Br_2$ *n*-Decanedicarboxy-*p*-bromoanilide (BARNICOAT), 2928.

$C_{24}H_{31}O_3N_2Cl$ Methyl*neo*brucidinium chloride (+H_2O) (GULLAND, PERKIN, and ROBINSON), 1650.

$C_{24}H_{31}O_3N_2I$ Brucidine methiodide (GULLAND, PERKIN, and ROBINSON), 1638.
Methyl*neo*brucidinium iodide (GULLAND, PERKIN, and ROBINSON), 1649.

$C_{24}H_{33}O_3N_2I$ Methyl*neo*dihydrobrucidinium iodide (GULLAND, PERKIN, and ROBINSON), 1659.

$C_{24}H_{33}O_4N_2I$ Tetrahydrobrucine methiodide (GULLAND, PERKIN, and ROBINSON), 1639.

$C_{24}H_{35}O_3N_2I$ Methoxymethyltetrahydrostrychnidine methiodide (CLEMO, PERKIN, and ROBINSON), 1618.

C_{25} Group.

$C_{25}H_{16}O_2$ Di-β-naphtha*spiro*pyran (DICKINSON and HEILBRON), 20.

$C_{25}H_{32}O_{11}$ *O*-Penta-acetyldihydrocarajuretinol (CHAPMAN, PERKIN, and ROBINSON), 3026.

$C_{25}H_{26}O_6$ Triphenylmethyl glucose, methylation of (HAWORTH, HIRST, MILLER, and LEARNER), 2443.

25 III

$C_{25}H_{17}O_2Cl$ 3-(β-2′-Hydroxy-1′-naphthylvinyl)-β-naphthapyrylium chloride (DICKINSON and HEILBRON), 19.

$C_{25}H_{19}O_3N_3$ Ketopiperonylethyldibenzodihydronaphthyridine (HAWORTH and PINK), 2347.

$C_{25}H_{18}O_6N_2$ *o*-Nitrobenzylidene-*N*-β-piperonylethylhomophthalimide (HAWORTH and PINK), 2347.

$C_{25}H_{23}O_3N_3$ Ketopiperonylethyldibenzohexahydronaphthyridine (HAWORTH and PINK), 2348.

$C_{25}H_{25}N_2I$ 1:1′-Diethylcarbocyanine iodides (HAMER), 2800.

$C_{25}H_{23}O_5N_3$ 3-*mp*-Dimethoxyphenyl-5-*mp*-dimethoxystyryl-Δ^5-*cyclo*hexen-1-one semicarbazone (DICKINSON, HEILBRON, and IRVING), 1893.

$C_{25}H_{29}N_2I$ Hexamethylindocarbocyanine iodide (HAMER), 2804.

$C_{25}H_{32}O_4N_2$ *O*-Diacetylhexahydrostrychnine (OXFORD, PERKIN, and ROBINSON), 2404.

$C_{25}H_{32}O_6N_2$ Brucidine methohydrogencarbonate (+ $2H_2O$) (GULLAND, PERKIN, and ROBINSON), 1641.

$C_{25}H_{32}O_6N_2$ Nitromethoxymethyldihydrobrucidine (GULLAND, PERKIN, and ROBINSON), 1647.

$C_{25}H_{34}O_2N_2$ *n*-Nonanedicarboxytoluidides (BARNICOAT), 2928.
n-Undecanedicarboxyaniline (BARNICOAT), 2928.

$C_{25}H_{34}O_4N_2$ Methoxymethyldihydrobrucidine, and its hydriodide (GULLAND, PERKIN, and ROBINSON), 1642.

$C_{25}H_{34}O_5N_2$ Oxymethoxymethyldihydrobrucidine (GULLAND, PERKIN, and ROBINSON), 1643.

$C_{25}H_{34}O_6N_2$ Dioxymethoxymethyldihydrobrucidine (GULLAND, PERKIN, and ROBINSON), 1643.

$C_{25}H_{36}O_4N_2$ Methoxymethyltetrahydrobrucidine, and its salts (GULLAND, PERKIN, and ROBINSON), 1654.

25 IV

$C_{25}H_{32}O_2N_2Br_2$ *n*-Undecanedicarboxy-*p*-bromoanilide (BARNICOAT), 2928.

$C_{25}H_{32}O_2N_2I$ Methyl-ψ-brucidine methiodide (GULLAND, PERKIN, and ROBINSON), 1651.

$C_{25}H_{36}O_2N_2Cl_2$ Methoxymethyldihydrostrychnidine dimethochloride (CLEMO, PERKIN, and ROBINSON), 1607.

$C_{25}H_{36}O_2N_2I_2$ Methoxymethyldihydrostrychnidine dimethiodide (CLEMO, PERKIN, and ROBINSON), 1606.

$C_{25}H_{38}O_2N_2I_2$ Methoxymethyltetrahydrostrychnidine dimethiodide (CLEMO, PERKIN, and ROBINSON), 1620.

C_{26} Group.

$C_{26}H_{16}Cl_2$ 1:5-Dichloro-9:10-diphenylanthracene (BARNETT, COOK, and WILTSHIRE), 1732.

$C_{26}H_{16}Cl_4$ 1:5:9:10-Tetrachloro-9:10-diphenyl-9:10-dihydroanthracene (BARNETT, COOK, and WILTSHIRE), 1729.

$C_{26}H_{17}Cl$ 1-Chloro-9:10-diphenylanthracene (BARNETT, COOK, and WILTSHIRE), 1728.

$C_{26}H_{20}N_2$ 9:9′-Dimethyl-3:3′-dicarbazyl (MAITLAND and TUCKER), 1390.

$C_{26}H_{24}N_2$ *NN′*-Dimethyldiphenylbenzidine (MAITLAND and TUCKER), 1392.

$C_{26}H_{32}O_6$ 3-Methoxy-4-ethoxystyryl methyl ketone, dimeride (DICKINSON, HEILBRON, and IRVING), 1894.

26 III

$C_{26}H_{18}OCl_2$ 1:5-Dichloro-9:10-diphenyl-9:10-dihydroanthranol (BARNETT, COOK, and WILTSHIRE), 1732.

$C_{26}H_{18}O_2Cl_2$ 1:5-Dichloro-9:10-diphenyl-9:10-dihydroanthraquinol (BARNETT, COOK, and WILTSHIRE), 1728.

$C_{26}H_{20}O_4N_6$ 3:3′-Dinitrobenzil osazone (CHATTAWAY and COULSON), 578.

$C_{26}H_{22}O_2N_2$ 1:8-Naphthalbisdimethylanilide (DAVIES and LEEPER), 1127.

$C_{26}H_{26}OSi_2$ Diphenylmethylsilicyl oxide (KIPPING), 106.

$C_{26}H_{36}O_2N_2$ *n*-Decanedicarboxytoluidides (BARNICOAT), 2928.

26 IV

$C_{26}H_{16}O_4N_2As_2$ 10:10′-Bis-4-carboxy-5:10-dihydrophenarsazine (BURTON and GIBSON), 249.

$C_{26}H_{18}O_8N_8S_2$ Dinitrodibenzaldehyde disulphide di-*p*-nitrophenylhydrazones (HODGSON and BEARD), 2424.

$C_{26}H_{22}O_8N_4S_2$ 3:3′-Dinitro-4:4′-di-*p*-toluenesulphonamidodiphenyl (BELL and ROBINSON), 1130.

$C_{26}H_{37}O_4N_2Cl$ Methoxymethyl dihydrobrucidine methochloride (GULLAND, PERKIN, and ROBINSON), 1645.

$C_{26}H_{37}O_4N_2I$ Methoxymethyldihydrobrucidine methiodide (GULLAND, PERKIN, and ROBINSON), 1643.

$C_{26}H_{37}O_6N_2I$ Dioxymethoxymethyldihydrobrucidine methiodide (GULLAND, PERKIN, and ROBINSON), 1648.

$C_{26}H_{39}O_4N_2I$ Methoxymethyltetrahydrobrucidine methiodide (GULLAND, PERKIN, and ROBINSON), 1655.

$C_{26}H_{40}O_8N_2S$ Methoxymethyldihydrobrucidine methosulphate (GULLAND, PERKIN, and ROBINSON), 1645.

26 VI

$C_{26}H_{56}O_9N_2Cl_6S_2Pt_2$ Tetrachloro(triaminopropane-camphor-β-sulphonate) platinum semihydrate (MANN), 1228.

C_{27} Group.

$C_{27}H_{16}Cl_2$ 1:5-Dichloro-9-phenyl-10-benzylanthracene (BARNETT, COOK, and WILTSHIRE), 1732.

$C_{27}H_{20}O_2$ 3:3′-Dimethyldi-β-naphtha*spiro*pyran (DICKINSON and HEILBRON), 1703.

$C_{27}H_{22}N_2$ 2:4-Diphenyl-5:6-(4′:5′:6′:7′-tetrahydroindole)(2′:3′)-quinoline (FAWCETT and ROBINSON), 2259.

$C_{27}H_{33}N_3$ *pp′*-Tetramethyldiaminodiphenyl-α-naphthylmethylamine (RODD and LINCH), 2178.

$C_{27}H_{30}O_7$ Ethyl 3-*mp*-dimethoxyphenyl-5-*mp*-dimethoxystyryl-Δ^3-*cyclo*hexen-1-one-2-carboxylate (DICKINSON, HEILBRON, and IRVING), 1892.

$C_{27}H_{30}O_{16}$ Rutin (ATTREE and PERKIN), 236.

27 III

$C_{27}H_{18}O_6N_4$ Triphthalimidotrimethylamine (KIPPING and MANN), 529.

$C_{27}H_{20}OCl_2$ 1:5-Dichloro-9-phenyl-10-benzyl-9:10-dihydroanthranol (BARNETT, COOK, and WILTSHIRE), 1732.

$C_{27}H_{22}O_2N_2$ Dioxydiphenyltetrahydroindoloquinoline (FAWCETT and ROBINSON), 2260.

$C_{27}H_{24}ON_2$ Phenyl α-tetrahydrocarbazylamino(6)-styryl ketone (FAWCETT and ROBINSON), 2259.

$C_{27}H_{24}O_3N_{10}$ Triphthalylhydrazidotriaminotrimethylamine (KIPPING and MANN), 529.

$C_{27}H_{25}N_2I$ 1:1′-Diallyl-4:4′-carbocyanine iodide (HAMER), 2802.

$C_{27}H_{27}ON_3$ *p*-Benzyl-*n*-butylaminobenzeneazo-β-naphthol (REILLY and DRUMM), 1396.

$C_{27}H_{28}N_2O$ *pp′*-Tetramethyldiaminodiphenylnaphthylcarbinols (RODD and LINCH), 2178.

$C_{27}H_{33}N_2I$ Tetramethyldiethylindocarbocyanine iodide (HAMER), 2804.

$C_{27}H_{32}O_2N_2$ *n*-Undecanedicarboxytoluidides (BARNICOAT), 2928.

27 IV

$C_{27}H_{39}O_4N_2I$ Ethoxymethyldihydrobrucidine methiodide (GULLAND, PERKIN, and ROBINSON), 1649.

$C_{27}H_{40}O_4N_2I_2$ Methoxymethyl dihydrobrucidine dimethiodide (GULLAND, PERKIN, and ROBINSON), 1645.

$C_{27}H_{42}O_4N_2Cl_2$ Methoxymethyltetrahydrobrucidine dimethochloride (GULLAND, PERKIN, and ROBINSON), 1657.

$C_{27}H_{42}O_4N_2I_2$ Methoxymethyltetrahydrobrucidine dimethiodide (GULLAND, PERKIN, and ROBINSON), 1656.

$C_{27}H_{42}O_{10}N_2S_2$ Methoxymethyldihydrostrychnidine dimethosulphate (CLEMO, PERKIN, and ROBINSON), 1605.

$C_{27}H_{44}O_{10}N_2S_2$ Methoxymethyltetrahydrostrychnidine dimethosulphates (CLEMO, PERKIN, and ROBINSON), 1619.

C_{28} Group.

$C_{28}H_{16}O_6$ Dibenzoylalizarin (GREEN), 2931.

$C_{28}H_{20}O_2$ 3:3′-Trimethylenedi-β-naphtha*spiro*pyran (DICKINSON and HEILBRON), 1704.

$C_{28}H_{24}N_2$ 9:9′-Diethyl-3:3′-dicarbazyl (MAITLAND and TUCKER), 1390.

$C_{28}H_{26}O_2$ Diphenyldi-o-tolylpinacol (BOYD and HATT), 905.

$C_{28}H_{34}O_5$ 3-*m*-Methoxy-*p*-propoxyphenyl-5-*m*-methoxy-*p*-propoxystyryl-Δ^5-*cyclo*hexen-1-one (DICKINSON, HEILBRON, and IRVING), 1895.

28 III

$C_{28}H_{18}O_6N_6$ *p*-Azoxydinitrostilbenes (NISBET), 2085.

$C_{28}H_{20}O_5N_4$ *p*-Azoxy-2-nitrostilbene (NISBET), 2085.

$C_{28}H_{21}O_2Cl$ 4-2′-Hydroxy-1′-naphthylidene-1:2:3:4-tetrahydro-8:9-benzoxanthylium chloride (DICKINSON and HEILBRON), 1704.

$C_{28}H_{22}O_3S_4$ 2-*p*-Methoxyphenyl-1:3-benzdithiole 2-oxide (HURTLEY and SMILES), 536.

$C_{28}H_{22}ON_2$ *p*-Azoxystilbene (NISBET), 2084.

$C_{28}H_{29}O_4Cl$ Ethyl 4-*o*-chlorostyracyl-2-phenyl-1:4-benzopyran-3-carboxylate (HEILBRON and HILL), 923.

$C_{28}H_{24}O_3N_2$ 2-*o*-Carboxybenzoyldi-*p*-tolyl ether phenylhydrazone (REILLY and DRUMM), 2817.

$C_{28}H_{25}O_4N_3$ Dibenzoyl derivative of substance $C_{14}H_{19}ON_2$ (KRISHNAMURTI and DEY), 1351.

$C_{28}H_{28}O_4N_2$ Strychnic benzoic anhydride (OXFORD, PERKIN, and ROBINSON), 2409.

$C_{28}H_{34}O_4N_2$ Psychotrine, hydrogen oxalate of (BRINDLEY and PYMAN), 1074.

$C_{28}H_{47}ON$ *iso*Erucic anilide (MIRCHANDANI and SIMONSEN), 375.

28 IV

$C_{28}H_{24}O_4N_2Se_2$ Di-*o*-benzoylmethylaminodiphenyl diselenide (CLARK), 2807.

$C_{28}H_{33}O_{12}N_5Co$ Nitrophenolnitrophenoxobisethylenediamminocobaltic nitrophenoxides (DUFF and BILLS), 2372.

C_{29} Group.

$C_{29}H_{28}N_2$ 4:4′-Tetramethyldiaminodiphenylmethyleneacenaphthene (RODD and LINCH), 2187.

$C_{29}H_{54}O_{16}$ Hendecamelezitose (LEITCH), 591.

29 III

$C_{29}H_{22}O_3N_4$ Triphthalimidotrimethylamine (KIPPING and MANN), 528.

$C_{29}H_{29}N_2Br$ 6:6′-Dimethyl-1:1′-diallyl-2:2′-carbocyanine bromide (HAMER), 2801.

$C_{29}H_{29}N_2I$ 6:6′-Dimethyl-1:1′-diallyl-2:2′-carbocyanine iodide (HAMER), 2801.

$C_{29}H_{30}ON_2$ 4:4′-Tetramethyldiaminodiphenylacenaphthenylcarbinol (RODD and LINCH), 2187.

$C_{29}H_{36}O_4N_2$ Emetamine, and its salts (BRINDLEY and PYMAN), 1075.

$C_{29}H_{38}O_4N_2$ *O*-Methylpsychotrine, and its picrate (BRINDLEY and PYMAN), 1072.

$C_{29}H_{49}ON$ *iso*Erucic *p*-toluidide (MIRCHANDANI and SIMONSEN), 375.

C_{30} Group.

$C_{30}H_{62}$ *n*-Triacontane, oxidation of (FRANCIS and WOOD), 1897.

30 II

$C_{30}H_{22}O_5$ 4′-Hydroxyflavanhydrone (IRVINE and ROBINSON), 2090.

$C_{30}H_{32}O_7$ Trianhydrobisbenzoylacetaldehydephloroglucinol (PRATT, ROBERTSON, and ROBINSON), 1976.

$C_{30}H_{28}N_2$ 4:4′-Tetramethyldiaminodiphenylmethylenefluorene (RODD and LINCH), 2187.

$C_{30}H_{30}O_2$ Tetra-*o*-tolylpinacol (BOYD and HATT), 908.

$C_{30}H_{60}O$ Ketone, from oxidation of *n*-triacontane (FRANCIS and WOOD), 1901.

$C_{30}H_{60}O_2$ Alcohol, from oxidation of *n*-triacontane (FRANCIS and WOOD), 1901.

30 III

$C_{30}H_{30}O_5N_4$ *p*-Azoxy-2-nitro-3′:4′-methylenedioxystilbene (NISBET), 2085.

$C_{30}H_{32}O_{11}N_6$ *p*-Azoxy-2:6-dinitro-4′-methoxystilbene (NISBET), 2085.

$C_{30}H_{24}O_3N_4$ *p*-Azoxybenzylidene-*p*-aminoacetophenone (NISBET), 2084.

$C_{30}H_{34}O_7N_4$ *p*-Azoxy-2-nitro-4′-methoxystilbene (NISBET), 2085.

$C_{30}H_{30}O_2N_4$ 2:2′-Dibenzamidotetramethylbenzidine (BELL and ROBINSON), 1698.

30 IV

$C_{30}H_{24}O_2N_2S_2$ *oo*′-Dicinnamamidodiphenyl disulphide (MILLS and WHITWORTH), 2747.

$C_{30}H_{34}O_4N_4S_2$ 2:2′-Di-*p*-toluenesulphonylamidotetramethylbenzidine (BELL and ROBINSON), 1698.

30 V

$C_{30}H_{24}O_2N_2Br_2S_2$ *oo*′-Dicinnamamidodibromodiphenyl disulphide (MILLS and WHITWORTH), 2747.

C_{31} Group.

$C_{31}H_{24}O_4$ Ethyl di-*p*-naphtha*spiro*pyran-3:3′-dicarboxylate (DICKINSON and HEILBRON), 1704.

31 III

$C_{31}H_{33}ON_3$ *pp′*-Tetraethyldiaminodiphenyl-β-naphthylcarbinol (RODD and LINCH), 2178.

31 IV

$C_{31}H_{42}O_4N_2I_2$ Emetamine dimethiodide (BRINDLEY and PYMAN), 1076.

C_{32} Group.

$C_{32}H_{23}Cl$ 10-Chloro-9:9:10-triphenyl-9:10-dihydroanthracene (BARNETT, COOK, and NIXON), 511.

$C_{32}H_{28}O_7$ 4′-Hydroxy-8-methoxyflavanhydrone (IRVINE and ROBINSON), 2091.

32 III

$C_{32}H_{21}O_4Sb$ Triphenylstibine dibenzoate (CHALLENGER and WILSON), 212.

$C_{32}H_{30}O_5N_6$ *p*-Azoxy-2-nitro-4′-dimethylaminostilbene (NISBET), 2086.

$C_{32}H_{21}O_4Bi$ Triphenylbismuthine dibenzoate (CHALLENGER and WILSON), 212.

C_{33} Group.

$C_{33}H_{30}O_5$ 3:3′-Dimethoxy-4:4′-dibenzyloxydistyryl ketone (DICKINSON, HEILBRON, and IRVING), 1896.

C_{34} Group.

$C_{34}H_{30}O_8$ 3:4:6:3′:4′:6′-Hexamethoxydianthrone (MACMASTER and PERKIN), 1309.

$C_{34}H_{40}N_4$ Octamethyltetra-aminotetraphenylethylene (RODD and LINCH), 2186.

$C_{34}H_{42}O_{20}$ Xanthorhamnin (ATTREE and PERKIN), 236.

$C_{34}H_{46}O_4$ Dimethyl diphenate (BELL and ROBINSON), 1698.

34 III

$C_{34}H_{42}ON_4$ Octamethyltetra-aminotetraphenylethanol (RODD and LINCH), 2186.

34 IV

$C_{34}H_{24}O_{15}N_4S_4$ Azoxy-derivative of *m*-aminobenzoyl-1-naphthylamine-3:6-disulphonic acid, sodium salt (BALABAN and KING), 3079.

C_{35} Group.

$C_{35}H_{26}O_{15}N_4S_4$ *s*-Carbamide of aminobenzoylnaphthylaminedisulphonic acid, sodium salt (BALABAN and KING), 3089.

$C_{35}H_{28}O_{17}N_2S_4$ *s*-Carbamide of 2-*m*-aminobenzoylamino-8-naphthol-3:6-disulphonic acid, salts (BALABAN and KING), 3094.

$C_{35}H_{26}O_{17}N_4S_4$ *s*-Carbamide of 1-*m*-aminobenzoylamino-8-naphthol-3:6-disulphonic acid, sodium salt (BALABAN and KING), 3092.

$C_{35}H_{25}O_{21}N_4S_6$ *s*-Carbamide of *m*-aminobenzoyl-1-naphthylamine-4:6:8-trisulphonic acid, sodium salt (BALABAN and KING), 3097.

C_{36} Group.

$C_{36}H_{22}N_2$ Substance, from oxidation of carbazole (MCLINTOCK and TUCKER), 1221.

C_{37} Group.

$C_{37}H_{30}O_6N_2$ Benzylidenebisbenzoylmandelamides (INGHAM), 696.

37 IV

$C_{37}H_{43}O_2N_6As_2$ *s*-Carbamido-3-*m*-aminobenzamido-4-piperidinophenylarsinic acid, and its salts (KING), 1055.

C_{38} Group.

$C_{38}H_{42}N_4$ *aa*-4:4′-Tetramethyldiaminodiphenyl-*ββ*-4:4′-tetramethyldiaminodiphenylethylene (RODD and LINCH), 2186.

38 III

$C_{38}H_{50}ON_4$ *aa*-4:4′-Tetraethyldiaminodiphenyl-*ββ*-4:4′-tetramethyldiaminodiphenylethan-*a*-ol (RODD and LINCH), 2186.

aa-4:4′-Tetramethyldiaminodiphenyl-*ββ*-4:4′-tetraethyldiaminodiphenylethan-*a*-ol (RODD and LINCH), 2186.

C_{39} Group.

$C_{39}H_{28}$ 9:9-Diphenyl-10:10-diphenylmethylene-9:10-dihydroanthracene (BARNETT, COOK, and NIXON), 511.

C_{40} Group.

$C_{40}H_{34}O_2$ *s-oo′*-Dibenzylbenzpinacol (BARNETT, COOK, and NIXON), 509.

C_{49} Group.

$C_{49}H_{36}O_{17}N_6S_4$ *s*-Carbamide of diaminobenzoyl-2-naphthylamine-6:8-disulphonic acid, salts (BALABAN and KING), 3089.

$C_{49}H_{36}O_{19}N_6S_4$ *s*-Carbamides of *m′*-aminobenzoyl-*m*-aminobenzoylamino-8-naphthol-3:6-disulphonic acids, salts (BALABAN and KING), 3095.

$C_{49}H_{36}O_{23}N_6S_6$ *s*-Carbamide of diaminobenzoyl-1-naphthylamine-4:6:8-trisulphonic acid, salts (BALABAN and KING), 3097.

C_{52} Group.

$C_{52}H_{38}$ Tetraphenyltetrahydrodianthranyl (BARNETT, COOK, and NIXON), 510.

C_{60} Group.

$C_{60}H_{50}O_2Si_4$ Diphenoxyoctaphenylsilicotetrane (KIPPING), 2732.

ERRATA.

VOL., 1926.

Page	Line	
1995	17	*for* "WILLIAM" *read* "WINSTON."

VOL., 1927.

531	13*	for "*Part XV*" read "*Part XVII.*"
1205	9	*for* "whom he also recommended as his successor" *read* "who is (as well as W. J. de Haas) one of his successors."
1226	Formula V	Insert "$(SCN)_2$" outside the bracket.
2169	Line 22	*for* "280° 189° 250° 250°." *read* ">280° 189° >250° >250°."
2856	26	*for* "boiling acetic acid" *read* "acetic acid."

* From bottom.

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